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DIELECTRIC POLARISATION AND THE FORM OF THE CARBON DIOXIDE MOLECULE.

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Received December 1, 1937.

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

Introduction.

Ibbs and Wakemann,[1] from their results on thermal diffusion of mixtures of gases containing *carbon dioxide* and on the temperature variation of viscosity of *carbon dioxide*, have concluded that "the molecules of *carbon dioxide* are of two definite kinds depending upon the temperature," and that "the *soft* low temperature molecule corresponds to a straight model while the *harder* high temperature molecule corresponds to a bent model". They deduced from their curves the temperatures of transition as 140° and 145° C. from the viscosity and the thermal diffusion data respectively. They have compared their results on thermal diffusion of the mixture of *hydrogen* and *carbon dioxide* and of other mixtures containing *carbon dioxide* with those of Lugg,[2] Elliott and Masson[3] and their viscosity values of pure *carbon dioxide* with those of Obermeyer,[4] Breitenbach[5] and Trautz and Kurz,[6] and have found similar points of singularity in the curves, though the actual temperatures of transition differ somewhat for the reasons given in their papers.

If the molecule does really undergo a change into the bent structure, the new form should be polar and consequently would have a higher electrical polarisation, the value of which should thereafter show a change with temperature. Accurate measurements of electrical polarisation at 100° and 183° C. have been made by Stuart,[7] who finds no change in the values at

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[1] Ibbs and Wakemann, *Proc. Roy. Soc.*, (A), 1932, **134**, 613–42.

[2] J. W. H. Lugg, *Phil. Mag.*, 1929, **8**, 1019.

[3] G. A. Elliott and I. Masson, *Proc. Roy. Soc.*, (A), 1925, **108**, 378.

[4] A. v. Obermeyer, *Wien. Ber.*, 1875, **71**, 281.

[5] P. v. Breitenbach, *Ann. Phys. Chem.*, 1899, **67**, 803.

[6] Trautz and Kurz, *Ann. Physik.*, 1931, **9**, 983.

[7] H. A. Stuart, *Z. Physik.*, 1928, **47**, 457.

the two temperatures. Since only one temperature above 145° C. has been employed, Ibbs and Wakemann have remarked that the results of Stuart cannot be taken as conclusive. It was therefore considered of great interest to measure the dielectric coefficients at different temperatures as accurately as possible. With this object in view, careful experiments were conducted in the range 80° to 200° C. The conclusion that the value of polarisation indicated no appreciable change, has already been published by the author in a recent note to *Current Science*.[8] Since the publication of that note, the measurements have been further extended to other temperatures below 80° C. and above 200° C. The details of measurements and of the results obtained form the subject of this present communication.

Experimental.

The chief difficulty in the work at high temperatures especially when dealing with small changes in capacity as in the case of gases, is to find a suitable steady bath. Generally, the vapour-baths have been employed in many cases. In the early measurements with *carbon dioxide*, attempts were made to employ a vapour-bath using nitrobenzene. In spite of all precautions taken to shield the container from air draughts and to provide the necessary insulation to minimise losses due to conduction and radiation, it was found that the individual readings were by no means steady and concordant. By taking a large number of readings, however, values could be obtained which nearly agreed with the more accurate ones obtained later by using a liquid-bath. Some additional difficulties were found when measurements at different temperatures were tried. Different liquids had to be used and accurate estimations of the stray capacities were found rather troublesome.

After several attempts, it was finally found that castor oil previously heated to about 250° C. for a few hours, served as a convenient bath-liquid. The heating was done by employing a " precision electric heater ", and the actual temperature of the bath was controlled by regulating the current. The copper-tubing enclosing the heater was wound into the form of a spiral just sufficient to take in the gas condenser. To secure greater uniformity of temperature, thick copper tubes were placed both on the outside and in the annular space of the gas condenser. These tubes were soldered together and in turn were soldered to the copper spiral enclosing the heater. This devise had to be made as any kind of a stirring arrangement was considered undesirable and unsuitable in such measurements. In order to

[8] K. L. Ramaswamy, *Curr. Sci.*, 1937, **5**, 152–53.

avoid the stray capacities due to the introduction of the metallic parts, the outer tubing of the heater was earthed.

The disposition of the rest of the apparatus and the details of experimental procedure were essentially the same as described in the earlier papers.[9]

Calibration.

It was found after conducting a series of measurements in which the individual readings were exceedingly concordant, that the values at the higher temperatures, though agreeing among themselves, came out far higher than that at the room temperature. These results are given in Table I, in which Column 1 represents the serial number and Columns 2, 3, 4 and 5 represent respectively the corrected temperature θg of the bath, the corrected difference of pressure $p_1 - p_2$ in mm., the mean pressure p_m in each experiment and the number of the individual readings taken. The sixth and the seventh columns give the values of $E-1 \times 10^6$ calculated to 760 mm. and 25°·0 C. and uncorrected and corrected for compressibility respectively. Any subsequent treatment given to the gas and other particulars are mentioned in the last column. In correcting the values at the ordinary temperature, the compressibility correction of 0·50 per cent. given by Cawwood and Patterson[10] and employed in the earlier investigations,[9] was adopted. For temperatures of 60° and 98° C., corrections of 0·4 and 0·2 per cent. were assumed. Since at still higher temperatures, the compressibility is negligible for the pressures employed, the values of $E-1$ in Column 7 are reproduced from column 6 directly.

The first few values obtained using the nitrobenzene vapour-bath are not given in the table as the results were exceedingly unsatisfactory. Only two values (Experiments 14*a* and 14*c*) are reproduced to indicate the degree of uncertainty with regard to the absolute values. Looking at the other values with the new arrangement, it is clear that the values at higher temperatures are distinctly larger than that at the room temperature. Even the room temperature value has changed from 900 (Experiments 15*a* and 15*b*) to 905 (Experiments 30, 31) clearly indicating that the gas was continuously getting contaminated with some impurity.

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[9] H. E. Watson, G. G. Rao and K. L. Ramaswamy, *Proc. Roy. Soc.*, (A), 1931, **132**, 569–86 ; *ibid.*, 1934, **143**, 558–88.

[10] Cawwood and Patterson, *J. Chem. Soc.*, 1933, p. 619.

TABLE I.

Values of $E - 1 \times 10^6$ *Calculated to* 760 *mm. and* 25°·0 *C. for Carbon Dioxide.*

Serial No.	θ_g °C.	$p_1 - p_2$ mm.	p mean mm.	No. of Readings	E−1	E−1 $\rho' = 0$	Remarks
14*a*	206·6	569·2	360	4	913·9	913·9	Nitrobenzene vapour bath.
c	,,	568·0	361	,,	918·2	918·2	,, ,,
15*a*	22·8	506·7	335	,,	904·6	900·6	Fractionally distilled at 20 mm.
b	,,	,,	,,	5	,,	900·6	and different sample of gas.
17	205·7	592·8	380	,,	915·1	915·1	
18	192·4	622·8	404	7	912·8	912·8	Castor oil bath
19	191·8	,,	,,	5	913·8	913·8	with electrical heating.
20	151·0	606·6	396	,,	912·8	912·8	
21	150·8	,,	,,	,,	914·6	914·6	
22	98·2	582·7	383	,,	917·5	915·7	
23	98·1	,,	,,	,,	917·9	916·1	
24	194·4	624·6	406	6	919·3	919·3	
25	194·8	624·8	,,	5	917·7	917·7	
26	152·1	607·2	396	,,	916·6	916·6	
27	151·6	607·0	,,	,,	915·7	915·7	
28	99·8	582·2	383	,,	915·1	913·3	
29	99·6	583·1	,,	,,	915·4	915·4	
30	24·9	538·5	360	,,	909·7	905·4	
31	,,	538·4	,,	,,	909·2	904·9	
32	25·4	574·0	383	,,	908·4	903·8	Gas refractionated at 50 mm. vapour
33	25·5	573·2	,,	,,	907·6	903·0	pressure.

TABLE I—(*Contd.*).

Serial No.	θg° C.	$p_1 - p_2$ mm.	p mean mm.	No. of Readings	E—1	$E-1_{p'=0}$	Remarks
34	24·4	571·8	381	7	910·7	905·7	Experiments tried with and without the mica covers for the bath. No change was detected.
35	95·1	617·4	405	8	913·4	911·5	
36	151·9	645·3	420	7	913·6	913·6	
37	199·3	664·4	430	,,	914·4	914·4	
38	171·2	652·6	424	9	915·5	915·5	
39	80·7	609·5	401	6	911·7	908·8	
40	134·0	637·7	416	,,	912·7	912·7	

Previous measurements[9] had clearly shown that there was no change in polarisation from $-80°$ to $+95°$ C. Further fractional distillations of the gas at low vapour pressures were made, which reduced this difference in the values of E $-$ 1 at the ordinary and higher temperatures, but not sufficiently to indicate that the difference was well within the limits of experimental error. During the course of these measurements it was at first thought that the heating coil when in circuit, might introduce stray capacities. Actual measurements of the values of the gas condenser with and without the heating coil in circuit were made and the results indicated no difference. It was then considered that the gas condenser itself might undergo a slight deformation when heated and thus cause a change in capacity. In order to test this, a series of measurements on the dielectric coefficients of pure dry *methane* (the same sample which was used in earlier measurements[9]) was made at different temperatures, the results of which are given in Table II. These results definitely indicated that no possible deformation of the measuring condenser at the higher temperature took place. They further showed that the stray capacities were not altered by the introduction of the electric heater.

It was therefore finally concluded that the sample of *carbon dioxide* had been contaminated and that more careful measurements were necessary in order to arrive at definite conclusions.

TABLE II.

Values of $E - 1 \times 10^6$ *Calculated to* 760 *mm. and* 25°·0 C. *for Methane.*

Serial No.	θ_g° C.	$p_1 - p_2$ mm.	p_m mm.	No. of Readings	$E-1_{uncorr.}$	$E-1_{p=0}$	Remarks
1	192·9	616·3	396	5	804·6	804·6	Refractionated
2	191·6	614·5	394	,,	805·8	805·8	
3	191·7	614·3	,,	,,	803·3	803·3	
4	150·0	598·2	385	,,	803·4	803·4	
5	149·4	596·7	,,	,,	804·8	804·8	
6	96·0	571·5	372	,,	804·3	804·3	
7	96·1	,,	371	,,	804·4	804·4	
8	24·9	529·2	349	,,	805·0	803·5	
9	,,	529·1	,,	,,	805·2	803·7	Refractionated

A fresh sample of *carbon dioxide* was therefore prepared by heating pure sodium bicarbonate (Kahlbaum's sample for analysis) in vacuum. The gas was carefully dried over phosphorous pentoxide and purified by the usual method of repeated fractional distillations at low vapour pressures. Before starting the measurements, the gas condenser was thoroughly baked in vacuum at 220° C. for several hours, the desorbed impurities being condensed in liquid air and later pumped off. In addition to this, the gas condenser was thoroughly washed with pure dry *carbon dioxide* a number of times. The apparatus was then thoroughly evacuated and left in vacuum for a day to see if any adsorbed impurity was still present. When no trace of any gas was found to be present, the purified sample of *carbon dioxide* was introduced and the measurements were carried out as already described in previous papers.[9]

It is necessary to mention here that the actual measurement of temperatures was made by a standard thermometer reading to 200° C., but graduated in fifths of a degree right up to 207° C. This thermometer had been calibrated at the Physikalisch Technischen Reichsanstalt and issued with a certificate. All the necessary corrections for the observed temperatures and pressures were applied.

Results and their Accuracy.

The results of measurements with the pure sample of *carbon dioxide* are recorded in Table III (A). In Table III (B) the mean values of $E-1 \times 10^6$ (rounded off to the nearest whole number) obtained from the most reliable measurements at the temperatures mentioned, are given.

The temperatures and pressures were actually read correct to 0°·2 C. and 0·05 mm. respectively, though for convenience the pressures are given to a tenth of a millimetre. One of the sources of error, is in the measurement of capacities, which could not be determined correct to more than 0·0002 $\mu\mu$F. As the difference of capacity at the highest temperature recorded (*i.e.*, 210°·6 C.) was only about 0·0940$\mu\mu$F, the upper limit of error due to this cause amounted to about two parts in a thousand in any one measurement. The second source of error resulted from temperature readings, the upper limit due to this cause being about one part in a thousand. The errors due to the creeping of frequency of the circuit, was eliminated by taking a number of readings at definite intervals of time with the condenser full of gas and empty or nearly empty and by adjustment of trickle charging current. The upper limit of error in the value of $E-1$ in any particular experiment, therefore, could not be more than three parts in a thousand. But since a large number of measurements were made, the accuracy in the calculated mean values of $E-1$ given in Table III (B) is far greater.

TABLE III (A).

Values of $E-1 \times 10^6$ *Calculated to* 760 *mm. and* 25°·0 C. *for Carbon Dioxide.*

Serial No.	θg° C.	p_1-p_2 in mm.	p mean mm.	No. of Readings	$E-1 \times 10^6$	$E-1_{\rho=0}$	Remarks
41 *a*	21·4	539·5	359	5	903·8	899·5	Passed over P_2O_5. Fractionated.
b	,,	539·6	,,	,,	902·3	898·0	
42 *a*	61·7	566·0	373	,,	903·4	899·8	
b	61·3	,,	,,	,,	902·3	898·7	
43 *a*	98·9	573·5	375	,,	903·6	901·8	Passed over P_2O_5. A bubble of incondensible fraction removed.
b	98·0	573·2	,,	,,	904·2	902·8	

TABLE III (A)—(*Contd.*).

Serial No.	θ_g° C.	$p_1 - p_2$ in mm.	p mean mm.	No. of Readings	E−1× 10^6	E−1 $_{p=0}$	Remarks
44 *a*	135·3	583·6	379	6	901·0	901·0	Passed over P_2O_5. No incondensible fraction.
b	134·8	583·4	,,	5	901·7	901·7	
45 *a*	147·6	582·4	378	6	900·2	900·2	,, ,, ,,
b	,,	582·9	,,	5	901·9	901·9	
c	147·2	582·7	,,	7	899·0	899·0	
46 *a*	21·8	527·7	351	5	902·9	898·7	,, ,, ,,
b	,,	,,	,,	6	903·6	899·4	
47 *a*	167·4	586·0	379	4	902·5	902·5	,, ,, ,,
b	169·5	,,	,,	3	899·1	899·1	
c	169·9	,,	,,	5	901·5	901·5	
d	169·7	586·8	,,	6	899·8	899·8	
48 *a*	210·6	598·0	385	4	899·8	899·8	Passed over P_2O_5. A trace of incondensible removed.
b	209·5	597·4	384	5	901·1	901·1	
c	,,	,,	,,	,,	896·2	896·2	
d	208·5	,,	,,	2	898·2	898·2	,, ,, ,,
49 *a*	21·7	584·5	392	5	902·5	897·8	No incondensible fraction.
b	,,	,,	,,	4	904·4	899·7	
c	22·2	584·0	,,	6	904·8	899·8	
50 *a*	60·8	610·8	406	5	900·8	897·1	,, ,, ,,
b	60·4	610·6	,,	,,	902·5	898·8	
51 *a*	189·8	673·5	439	7	899·3	899·3	,, ,, ,,
b	,,	,,	,,	6	895·2	895·2	Somewhat unsteady.
c	,,	,,	,,	5	899·1	899·1	Very steady.

TABLE III (B).

Mean Values of E−1 *at* 760 *mm. and* 25°·0 C. *for* CO_2.

Serial No.	$\theta°_g$ C.	No. of Expts.	No. of Reading	E—1 (Mean)
1	22	7	36	899
2	61	4	20	899
3	99	2	10	902
4	135	„	11	901
5	147	3	18	900
6	169	4	„	901
7	190	3	„	899
8	210	4	16	900

Discussion.

The structure of the molecule of *carbon dioxide* like *nitrous oxide*, has been the subject of numerous publications dealing with different aspects of the problem of molecular structure. It is neither necessary nor possible to go into the discussion of all the data published so far, since many of the properties dealt with have not been studied at the higher temperatures, at which the change in structure is supposed to take place. The preponderance of evidence from data on Raman spectra, ultra-violet and infra-red absorption spectra, Kerr constant, and specific heats are all in favour of a symmetrical linear structure for the molecule at the ordinary temperatures. The present careful series of measurements on dielectric cofficients from + 20° to + 210° C. has clearly shown that the possibility of any change into a bent form is excluded. Similar measurements on dielectric coefficients at higher temperatures by Stuart[7] lead to the same conclusion. It may be mentioned here that the earlier measurements[9,11] carried out from − 80° to + 95° C., have also shown that the gas is non-polar and so posesses a symmetrical linear structure.

[11] K. L. Ramaswamy, *Proc. Ind. Acad. Sci.*, (A), 1935, **4**, 365.

If the molecule does really undergo a change into the bent structure, one should observe a change also in the molar refraction, though of a very small magnitude. This aspect of the problem has been carefully investigated recently by Goldschmidt and Hölemann,[12] who have found that the refractivity of carbon dioxide is constant right up to 400° C., above which temperature a measurable change occurs. This conclusion is again in agreement with a linear model.

Regarding the temperature of a possible transformation into the bent structure, the results are extremely discordant. Ibbs and Wakemann[1] have given 140° C. and 145° C. from viscosity and thermal diffusion data. Lugg's[2] results on thermal diffusion gives the temperature as 204° C., while McCrae[13] from considerations of specific heats suggests that the change from the bent to the straight type should occur below 0° C. Recently Van Cleave and Maass[14] have made some measurements on the viscosities of gases and have found that the occurrence of an inversion point in the curve representing η/T against temperature, is associated with the presence of a dipole moment. According to these authors, carbon dioxide shows a point of inflection at 12° C. and possesses an electric moment of 0·13. The reason why the authors have adopted the moment of 0·34 for *propylene* given by us[9] and not considered the zero value for the moment of *carbon dioxide* mentioned in the same paper, is not clear. It appears, however, that further careful experiments are necessary to decide this point.

In conclusion, it may be mentioned that the measurements of dielectric polarisations from + 20° to + 210° C. recorded in this communication and those from − 80° to + 25° C. and + 25° to + 95° C. recorded in the previous publications,[9,11] all clearly indicate that the molecule of *carbon dioxide* is non-polar within the temperature range of − 80° to + 210° C. These results definitely show that the molecule must have a symmetrical linear structure and do not support the possibility of a bent model above 145° C. as postulated by Ibbs and Wakemann.[1]

Summary.

1. Accurate measurements of the dielectric coefficient of *carbon dioxide* have been made at 8 different temperatures from + 20° to + 210° C.

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[12] H. Goldschmidt and P. Hölemann, *Z. Physik. Chem.*, 1936, **B32**, 341–52.

[13] McCrae, *Proc. Camb. Phil. Soc.*, 1927, **23**, 890 ; *ibid.*, 1928, **24**, 290.

[14] A. B. Van Cleave and O. Maass, *Can. J. Research*, 1935, **13B**, 140–8.

2. The value of polarisation is constant within the limits of experimental error, indicating that the gas is non-polar within the temperature range employed.

3. The results of the present investigations do not support the possibility of a bent structure for the molecule of *carbon dioxide* above 145° C., as postulated by Ibbs and Wakemann from their measurements on thermal diffusion and viscosity.

4. Incidentally, accurate measurements of the dielectric coefficients of *methane*, have been made at four different temperatures in the range from + 25° to + 190° C.

In conclusion, I wish to record my grateful thanks to Professor Sir C. V. Raman, Kt., F.R.S., N.L., for his kind interest in this work.

THE ELECTRICAL CONDUCTIVITY OF POTASSIUM CHLORIDE IN METHYL ALCOHOL-WATER MIXTURES.

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Received May 31, 1937.

(Communicated by Prof. K. C. Pandya, M.A., Ph.D., D.I.C.)

R. N. Agarwala and D. C. Mandeville[1] examined the electrical conductivity of KCl in mixtures of water and acetone and various alcohols. They studied the water-acetone mixtures in particular. On plotting $\wedge c$ against $\sqrt{c}$ they obtained a series of definite maxima and minima. Methyl alcoholic solutions also gave curves showing some maxima and minima but there was no observable regularity about them. The object of the present investigation was to extend the work on methyl alcohol-water mixtures, particularly in dilute solutions.

The potassium chloride and methyl alcohol were analytical reagents: the latter contained about 0·05 per cent. of acetone as an impurity. Water for the conductivity determinations was prepared in a Hartley's still, the first and the last thirds being rejected. It had a specific conductivity of $1{\cdot}6 \times 10^{-6}$ r. ohms. The usual precautions were observed in storing and using all these substances. In order to ascertain whether the minute acetone content of the alcohol (*i.e.*, 0·05 per cent.) had any effect on the conductivity, the acetone content was raised to 0·01 per cent. in the 30 per cent. alcohol solutions and the conductivity measured. It was found that the change in conductivity was negligible.

A previously used cell of resistance glass, with bright platinum electrodes was employed. (Platinized electrodes promote the atmospheric oxidation of alcohol[2].) The resistances were measured by means of a Pye bridge. The source of alternating current was a thermionic valve oscillator of frequency 1,250 cycles per second. Temperature was kept constant at 25 ± ·05° C. by means of a thermostat with a Lowry regulator.

The solutions were made up as follows:—

The required quantities of non-electrolyte and of a solution of potassium chloride of known concentration were mixed and made up to 50 c.c. in a graduated flask by the addition of conductivity water. The solution was then transferred to the cell which was allowed to remain in the thermostat

for about twenty minutes to attain the proper temperature, before resistance was measured.

Experimental Results.

% of alcohol	0	5	10	20	30	40	60	80	90
Specific conductivity of mixture in r. ohms × 10^6	1·6	2·3	3·21	4·24	4·82	5·17	6·43	9·14	10·6

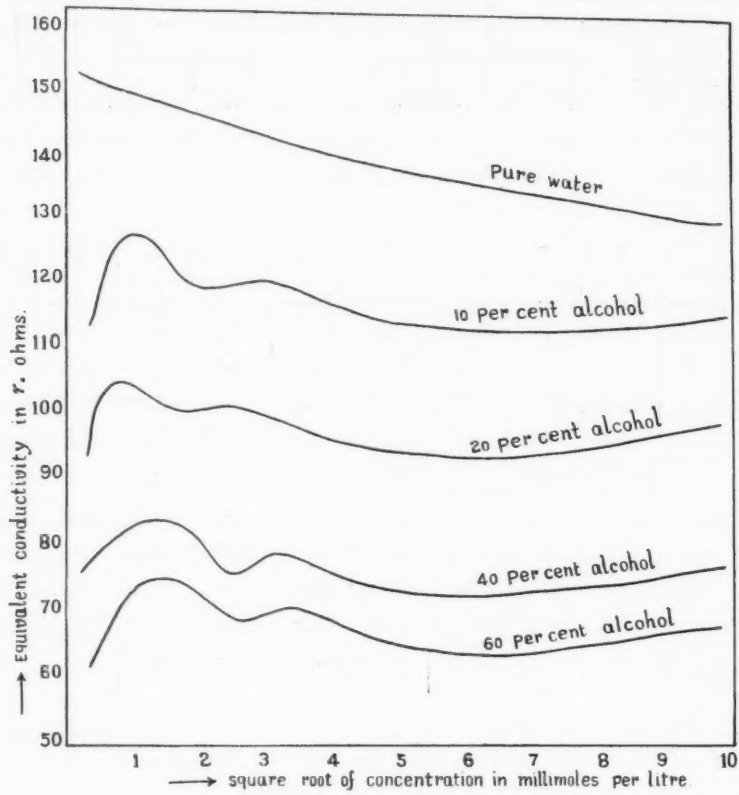
Equivalent Conductivity of Aqueous Alcoholic Solutions of KCl in r. ohms.

Percentage of Alcohol	0	5	10	20	30	40	60	80	90
M/10 KCl	128·62	..	115·5	99·65	84·0	77·45	68·16	64·06	61·95
M/20 ,,	133·1	119·79	112·5	95·08	82·69	73·96	64·0	61·34	65·36
3M/100 ,,	135·9	121·0	112·8	94·5	83·7	74·1	64·09	62·3	69·97
M/50 ,,	138·0	124·0	114·7	95·0	84·5	74·5	66·2	63·7	71·72
M/100 ,,	141·18	128·3	119·0	98·62	86·0	79·42	71·05	66·91	74·7
M/200 ,,	143·8	129·1	118·4	100·48	88·5	75·70	68·82	67·9	78·44
M/500 ,,	146·3	132·5	120·75	100·65	87·0	83·4	74·75	73·6	84·05
M/1000 ,,	147·4	137·1	126·0	103·4	89·6	82·5	72·25	71·18	83·8
M/5000 ,,	148·88	133·8	119·45	101·9	87·7	79·45	..	..	..
M/20000 ,,	149·5	128·78	110·06	91·96	80·36	76·0	59·0	43·5	71·8

The addition of methyl alcohol lowers the conductivity of aqueous solutions of potassium chloride. As the percentage of alcohol increases the conductivity decreases and it reaches a minimum value when the alcohol content of the medium is 70 to 80 per cent. by volume ; further additions of alcohol tend to increase the conductivity. This minimum is observed with all concentrations of KCl except the M/10 solution ; in the dilute solutions the effect is more marked.

If the conductivities are plotted against the square root of concentration (KCl) in any particular mixture of water and alcohol (*e.g.*, 20 per cent. alcohol and water) the curves obtained show maxima and minima at various KCl concentrations. The concentrations of KCl at which these maxima and minima occur are not fixed for all alcohol-water mixtures as was observed by Agarwala and Mandeville (*loc. cit.*) for acetone-water mixtures, but

depend also on the alcohol content of the particular mixture. The equivalent conductivity decreases with increasing dilutions after M/1000 KCl in all alcohol-water mixtures (see graph).



Discussions.

The lowering of the equivalent conductivity on the addition of alcohol is at least partly due to the change in viscosity. The viscosity increases with the addition of alcohol until a maximum is reached when the alcohol content of the medium is about 40–50 per cent. after which the viscosity decreases with increase of alcohol. In accordance with Walden's rule, conductivity decreases as the viscosity increases. But whereas the maximum in viscosity occurs when the alcohol content is about 50 per cent. by volume the minimum in the conductivity occurs when the alcohol content

is about 70–80 per cent. Obviously, some other factor besides viscosity is at work. The experimental observations most difficult to explain adequately are the maxima and minima obtained when conductivities in alcohol-water mixtures are plotted against $\sqrt{c}$. The simplest explanation is compound formation between the solvent and the ions. Kendall[3] has suggested that compound formation between solvent and solute is a process preliminary to ionisation. Water and methyl alcohol both contain the active-OH group, which can function either as a donor or as an acceptor of electrons. Hence they can associate with anions as well as with cations.

The collisions of the ions with one another will tend to oppose the formation of co-ordinate compounds, *i.e.*, solvation. The probability of an ion (simple or solvated) colliding with another is greater in the more concentrated solutions. As the concentration decreases a state will be reached when the collision probability just balances the tendency to solvation. The minima in the curves referred to above, are probably due to some such equilibrium state.

Now, solvation is in a sense quantised. An ion cannot be associated with anything but an integral number of solvent molecules. So, until the conditions have become favourable for the addition of one more molecule to the solvation sheath the conductivity will increase with dilution. When the conditions are favourable once again (at the maximum on the curve) further solvation takes place and the conductivity falls again. In fine, the anomalies may well be due to solvation in steps.

In conclusion, the authors desire to express their gratitude to Professors K. C. Pandya, H. Krall and B. L. Vaish for their assistance and the keen interest which they evinced in the work.

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GEOMETRICAL INVERSION IN THE ACIDS DERIVED FROM THE COUMARINS.

Part VI. The Behaviour of the Acids Derived from 4-Methylcoumarins.

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Though some work has been carried out regarding the influence of alkyl substituents on the behaviour of coumarins towards alkali, it does not seem to be adequate and the results are not very definite. Methyl groups present in the benzene ring, do not markedly affect the properties of the compounds since they exhibit the normal coumarin behaviour by dissolving in alkali to give almost colourless solutions which subsequently become yellow and later on develop a beautiful yellowish green fluorescence, which is taken as an indication of the formation of the coumaric acid. Alkyl groups present in the pyrone ring inhibit these colour effects. According to the observations of Hjelt[1] and Fries and his co-workers,[2] if alkyl groups should be present in the 3- and 4-positions, the opening of the lactone ring takes place more slowly and the corresponding coumarinic acids pass back into the coumarins more easily and quickly.

For the change of the coumarinic acids into the corresponding coumaric acids, the situation seems to be different. With aqueous alkali ordinary coumarinic acid and those containing alkyl groups in the benzene ring go into the coumaric acids only very slowly. With 4-methylcoumarin the change is said to be quicker whereas with 3 : 4-dialkylcoumarins, under similar conditions, no coumaric acid is said to be produced. As for the reverse change Fries and Klostermann[2] found that β : 4-dimethyl and β : 5-dimethylcoumaric acids in glacial acetic acid solution, when treated with concentrated hydrochloric acid at the ordinary temperature changed completely in a few hours to the corresponding dimethylcoumarins. Coumaric and 4-methylcoumaric acids, on the other hand, remained unchanged even after a day. Similar differences were noted even when sulphuric acid was employed.

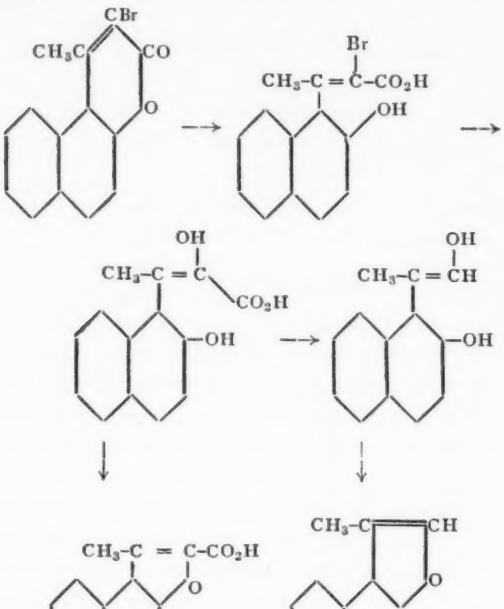
Dey and his co-workers[3] have isolated a number of fairly stable acids from 4-methyl-β-naphthopyrone and its derivatives by the action of alcoholic

potash and have attributed the *cis*-configuration to them for the following reasons: (1) The acids could be easily reconverted into the original pyrones, the change being brought about by simply passing dry hydrogen chloride through their suspension in acetic acid or by dissolving in concentrated sulphuric acid and pouring the solution into water. (2) They eliminate water at their melting points and are transformed into the corresponding coumarins. (3) The 3-chloro and bromoderivatives undergo change with alcoholic potash only slowly to give furan carboxylic acids.

Though they believe these properties to be peculiar to 4-methyl-β-naphthopyrone derivatives, a comparison with the acids derived from 4-methyl and 4 : 7-dimethylcoumarins seems to indicate that these are more or less general for all coumarins containing a methyl group in the 4-position. The question seems to be open as to whether they are *cis* or *trans* acids. Fries *et al.* considered the acids they obtained from 4-methyl and 4 : 7-dimethylcoumarins as *trans* acids which possess the peculiar property of closing up the ring easily, whereas Dey and his co-workers considered the acids derived from 4-methyl-β-naphthopyrone as *cis*-acids with remarkable stability. No unequivocal evidence seems to have yet been given in favour of either.

In one of the previous papers[4] of this series it has been shown that dehydrating agents like concentrated sulphuric acid and fuming hydrochloric acid produce the conversion of the coumaric acids into the coumarins, the yield of the products varying with the nature of the substituents in the acids. The acids derived from 4-alkylcoumarins seem to possess this property in a higher degree. Though normally coumaric acids do not close up the ring on simple heating, they do so in the presence of a little mercury compound.[4] Further the esters of coumaric acids all undergo conversion into the coumarins above their melting points.[5] This property of undergoing ring closure on heating therefore does not definitely indicate that the acids derived from 4-methylcoumarins are *cis*-acids. The third argument of Dey *et al.* is based on the assumption that the formation of furan carboxylic acids from 3-chloro or bromo coumarin by the action of potash involves the elimination of a molecule of hydrogen chloride or bromide as such and necessitates the existence of the two atoms concerned in close proximity. According to them, since the acid derived from 4-methyl-3-halogeno-β-naphthopyrone is *cis*, these two atoms are apart and hence their elimination is difficult. There seems to exist no support for this explanation. It is well recognised that elimination of halogens and hydrogen halides takes place more easily from the *trans* positions than from the *cis* and that several transformations such as the Beckmann's transformation involve *trans* positions. The action of potash on 3-bromo-4-methyl-β-naphthopyrone obviously proceeds through the

initial replacement of the halogen with a hydroxyl group and the subsequent elimination of water.



The isolation by Dey and Lakshminarayanan of the aldehyde[3] as a by-product supports this view clearly. Normally the hydroxy acid is stable and undergoes ring closure to the coumarilic acid whereas in the present case it partly undergoes decarboxylation to yield the aldehyde which undergoes further change into the furan only with difficulty. The arguments, therefore, in favour of *cis*-configurations for the acids are not decisive.

On the other hand, there is room for doubt if they are really *cis* acids. They are too stable to be *cis* and further they have not been converted into the *trans*, though ordinarily *cis* acids are readily converted into the stabler *trans* forms by well-known methods. The claim of Dey and Lakshminarayanan[3] to have isolated a second acid (*trans*) from 4-methyl-β-naphthopyrone does not seem to be correct. The new acid melts lower than the original '*cis*' acid and undergoes conversion into the pyrone much more readily. On examining this product carefully it is now found that it is a partially mercurated variety of the original acid and hence it melts lower and

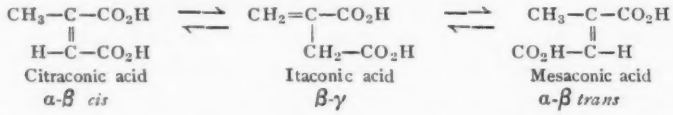
reacts more vigorously. The property of getting transformed into the pyrone by the action of ultra-voilet light or sunlight is possessed by the mercury-free acid melting at the higher temperature in a marked degree.

In view of the indefinite position outlined above, a detailed study of the coumarins containing a methyl group in the 4-position has been made with reference to their conversion into the corresponding *cis* and *trans* acids by the action of alkali. The following pyrones have been examined: (1) 4-methyl-β-naphthopyrone, (2) 4-methyl-α-naphthopyrone, (3) 4-methyl-7-hydroxycoumarin, (4) 4-methyl-7-methoxycoumarin and (5) 4 : 7-dimethylcoumarin. Amongst these the first undergoes the change into β-2-hydroxy-1-naphthylcrotonic acid very readily. Simple solution in cold alcoholic potash or hot aqueous potash and subsequent acidification is enough to produce the acid. Further boiling effects no further change. Mercuric oxide in the presence of sodium hydroxide produces mercuration of the acid very solwly. Otherwise it effects no isomeric change. The other pyrones in the list dissolve in alkali on simple treatment obviously to produce *cis* acids which get reconverted into the pyrones completely on acidification. Longer boiling with alkali or the use of catalysts like mercuric oxide produce acids which are fairly stable. Some of them can be crystallised from boiling alcohol. All these acids have the common property of undergoing easy conversion into the corresponding pyrones on being subjected to the action of heat or to the action of dehydrating agents. They do not undergo further transformations into stabler acids by continued boiling with aqueous alkali containing mercuric oxide. Under these conditions all known *cis* acids easily get converted into the *trans* compounds. It, therefore, seems to be incorrect to call them *cis* acids. They are really *trans* acids which have the characteristic of easy formation from the pyrones and easy conversion back into them.

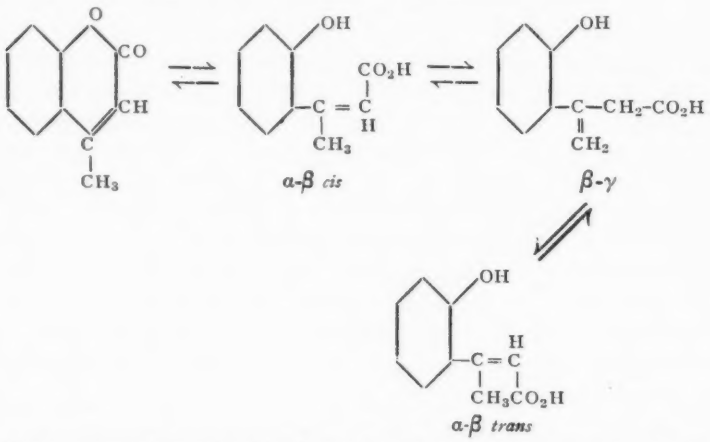
In further support of this view the methyl ethers of these compounds have been investigated in detail. The acids undergo methylation easily with dimethyl sulphate in alkaline solution to yield stable ethers. The same compounds are readily obtained from the pyrones by the action of dimethyl sulphate in the presence of aqueous alcoholic potash. Though easily formed, they are really *trans* ethers since they are markedly stable and do not undergo conversion into isomeric compounds by long treatment with acids or mercury compounds.[8] Hence the conclusion is drawn that these ethers and the corresponding hydroxy acids belong to the *trans* group.

The remarkable ease with which these *trans* acids are produced from the 4-methyl pyrones and the readiness with which they undergo conversion into the pyrones can be easily explained when it is realised that just as

in the case of citraconic and mesaconic acids, a facile tautomeric mechanism for interconversion exists in them. Linstead and Mann[7] have shown that with citraconic and mesaconic acids the configurational change in the α-β acids proceeds entirely through the intermediate formation and decomposition of the β-γ isomeride as follows :—



The velocity of the stereochemical change is rather high. This is also supported by the observation of Fittig and Kettner[8] in regard to dimethylmaleic and fumaric acids. Further it is a characteristic of this mechanism that it enables the *trans* to *cis* change to take place with ease. The following represents the change in the case of 4-methylcoumarins.



The tautomeric mechanism is not found to take place in aliphatic monocarboxylic acids. But in the case of the methylcoumarinic and coumaric acids the phenyl ring obviously performs the same function as the second carboxyl in citraconic and mesaconic acids. In this connection the similarity that exists between malonic and phenylacetic acids in possessing the reactive methylene group may be mentioned.

Regarding the effect of the methyl group in position 4, all observations indicate that *cis* acids cannot be isolated since they are very unstable and go over into the pyrones on the one hand or into the *trans* acids on the other very readily. The *trans* acids that are easily formed are not however very stable. Though unaffected by alkali they get converted into the coumarins

on being subjected to heat or dehydrating agents or acids. They form, therefore, a remarkable series of unstable *trans* acids.

Experimental.

Preparation of the 4-methylcoumarins.—Equimolecular quantities of the appropriate phenolic compound and ethyl aceto acetate were condensed in the presence of concentrated sulphuric acid. 4-methyl-α-naphthopyrone, 4-methylumbelliferone and 4 : 7-dimethylcoumarin were obtained very readily by the methods found in the literature. 4-methyl-β-naphthopyrone was produced in a rather poor yield by the method of Dey and Lakshminarayanan.[9] It has now been found that by reducing the amount of sulphuric acid the process is rendered simpler and the yield improved.

A mixture of finely powdered β-naphthol (14 g.) and ethyl acetoacetate (15 g.) was slowly added to concentrated sulphuric acid (16 c.c.) which was cooled under the tap. After allowing the mixture to stand overnight, it was poured into excess of crushed ice. The solid product was washed with water, subsequently shaken with dilute sodium hydroxide solution and crystallised from ethyl alcohol. It melted at 183°C. and the yield was about 8 grams.

The methylation of 4-methyl-7-hydroxycoumarin using methyl iodide or dimethyl sulphate and sodium hydroxide gave rise only to a poor yield of 4-methyl-7-methoxycoumarin due to the opening up of the pyrone ring and the formation of by-products. The process was therefore conducted in dry acetone medium using methyl iodide and anhydrous potassium carbonate. 4-Methyl-7-hydroxycoumarin (4 g.) was dissolved in dry acetone (100 c.c.), methyl iodide (7 c.c.) and anhydrous potassium carbonate (10 g.) added and the contents slowly refluxed on a water-bath for about five hours. The solvent was then distilled off, water added and the mixture stirred well in order to dissolve the alkali carbonate. The insoluble solid was filtered and crystallised from alcohol. It melted at 160° and the yield was 4 grams.

The trans *acids and their reactions. β-2-Hydroxy-1-naphthylcrotonic acid.*—This acid was prepared by Dey and Lakshminarayanan by boiling 4-methyl-β-naphthopyrone with aqueous alcoholic potash for four hours and the subsequent acidification of the alkaline solution after removing the alcohol. It is now found that the same acid could be obtained by simpler procedure.

(1) *Action of hot aqueous potash.*—The pyrone (2 g.) was dissolved in twenty per cent. aqueous potash (20 c.c.) by boiling for a few minutes, diluted with water to about 100 c.c. and cooled. The clear solution yielded

on acidification an almost theoretical yield of the crotonic acid which was purified by dissolution in sodium bicarbonate and subsequent crystallisation from alcohol.

(2) *Action of cold aqueous alcoholic potash.*—The pyrone (2 g.) was treated with alcohol (30 c.c.) and twenty per cent. aqueous potash (20 c.c.) and shaken. The substance went into solution rapidly. The clear solution was then diluted with water, acidified and the crystalline solid was purified as above. The yield was almost theoretical.

(3) *Action of mercuric oxide and cold alkali.*—The finely powdered pyrone (2 g.) was shaken in the cold for half an hour with aqueous caustic soda (2 g. in 50 c.c.) and yellow mercuric oxide (1 g.). The pyrone rapidly dissolved. After filtering off the mercuric oxide, the filtrate was first treated with hydrogen sulphide in order to remove any combined mercury and finally acidified. The precipitated acid was purified as above.

(4) *Action of mercuric oxide and hot aqueous alkali.*—Following the procedure of Dey and Lakshminarayanan,[3] a substance decomposing at about 112° was obtained. It however contained mercury (about five per cent.). It was therefore dissolved in caustic alkali and the mercury removed by passing hydrogen sulphide. After filtering off the mercuric sulphide, the clear filtrate on acidification gave the acid melting at 148° and found to be identical with the samples obtained by other methods. It was therefore concluded that the substance decomposing at 112° was a mixture of the acid with some mercurated sample of it.

The pure acid decomposes at 148° and crystallises from alcohol as colourless plates tapering at the ends. It is sparingly soluble in cold water and is more soluble in hot water. In acid medium it gets converted into the pyrones in the course of 24 hours. It is quite stable in alkali. The action of mercuric oxide in the cold or hot alkaline solution or of mercuric acetate in neutral solution produced no change except partial mercuration and when the combined mercury was removed with hydrogen sulphide, the original acid was recovered unchanged.

At the melting point, the acid evolves water and gets completely converted into pyrone. One gram of the acid in 25 c.c. of alcohol was exposed in a silica flask to sunlight. After about 8 hours the sparingly soluble pyrone began to crystallise out and after 24 hours exposure, the solvent was distilled off and the residue was found to be the pure pyrone melting at 183°. There remained no detectable amount of the original acid. Quite a similar behaviour was noted in the presence of ultra-voilet light, complete conversion taking place within 24 hours. Under the conditions described by Dey and

Lakshminarayanan[3] using chloroform as solvent, bromine as catalyst and ultra-voilet light as the source of energy, 60 per cent. of the acid melting at 148° underwent conversion into the pyrone whereas the impure acid melting at 112° changed almost completely into the pyrone, though the product had to be crystallised repeatedly before it could give the correct melting point of 4-methyl-β-naphthopyrone.

4-Hydroxy-β-methylcoumaric acid or β-2 : 4-dihydroxyphenylcrotonic acid.—4-Methyl-7-hydroxycoumarin (2 g.) was dissolved in about 50 c.c. of 0·5 per cent. aqueous sodium hydroxide and the cold solution shaken with yellow mercuric oxide (2 g.) for about an hour. Mercuration took place consuming a good amount of the mercuric oxide. The remaining oxide was filtered off and the filtrate treated with hydrogen sulphide in order to remove all combined mercury as sulphide. After filtering off the sulphide, the clear solution was acidified at 0°. The precipitated acid was purified by dissolving in aqueous sodium bicarbonate and reprecipitating at the temperature of melting ice. It sintered strongly at about 115° and melted at 185°. It could not be crystallised from boiling alcohol as it rapidly underwent change into the original pyrone. The solution of the acid in sodium bicarbonate or in sodium hydroxide gave a blue fluorescence.

4-Methoxy-β-methylcoumaric acid or β-2-hydroxy-4-methoxyphenylcrotonic acid.—This was prepared from 4-methyl-7-methoxycoumarin using alkali and mercuric oxide. About 2 g. of the coumarin were dissolved in hot 20 per cent. potassium hydroxide (30 c.c.). The solution was diluted to 100 c.c. with water, cooled and shaken with yellow mercuric oxide (2 g.) for about an hour. It was filtered, the filtrate treated with hydrogen sulphide in order to remove all combined mercury as mercuric sulphide and finally acidified. It was first purified by solution in sodium carbonate and reprecipitation and subsequently crystallised from aqueous alcohol. It was obtained as colourless rectangular plates melting at 145° with decomposition. [Found : C, 63·2 per cent.; H, 6·0 per cent. ; $C_{11}H_{12}O_4$ requires C, 63·5 per cent. ; H, 5·8 per cent.] The acid undergoes conversion into the coumarin with great ease on heating to its melting point and in the presence of concentrated hydrochloric and sulphuric acids in the cold. It is unaffected by prolonged reaction with alkali and mercuric oxide. It undergoes condensation with mercuric acetate rather readily but the product yields only the original acid on being decomposed with hydrogen sulphide.

β : 4-Dimethylcoumaric acid or β-2-hydroxy-4-methylphenylcrotonic acid.—4 : 7-Dimethylcoumarin undergoes conversion in boiling aqueous potash only very slowly. The acid could, however, readily be obtained by shaking with

alkali and mercuric oxide exactly as mentioned for 4-methyl-7-methoxy coumarin. It crystallised from dilute alcohol in the form of stout needles melting at 157° with decomposition (compare Fries and Klostermann[2]—142° decomp. and Perci[10]—136° decomp.). [Found C, 68·6 per cent.; H, 6·2 per cent.; $C_{11}H_{12}O_3$ requires C, 68·8 per cent.; H, 6·3 per cent.] It is sparingly soluble in water and readily in alcohol. It is also soluble in ether and acetone but not in chloroform, carbon disulphide or benzene. It is fairly stable in the presence of dilute alkali and dilute acid but with concentrated acids in the cold it undergoes conversion into the coumarin.

A sample of the acid was decomposed at its melting point (heating for about fifteen minutes at 160°). Though the product was completely insoluble in sodium bicarbonate and was therefore free from the original acid, it could not be easily crystallised from alcohol. One per cent. aqueous sodium hydroxide removed a small quantity of the impurity and the residue was found to be the pure pyrone which could now be easily crystallised. The alkali solution yielded on acidification a very small quantity of a substance giving a brown colour with ferric chloride. This was probably an indication that small quantities of the corresponding hydroxy-styrene are also formed.

When exposed to sunlight or ultra-voilet light in absolute alcoholic solution for twenty-four hours, it underwent complete conversion into the coumarin. On the other hand, mercury compounds in alkaline medium produced no change.

Preparation and properties of the ethers of the acids. β-2-Methoxy-1-naphthylcrotonic acid.—The hydroxy acid was dissolved in excess of dilute aqueous potash and methylated by shaking with excess of dimethyl sulphate in the cold for one hour. The excess of dimethyl sulphate was decomposed by heating for a short period at 100° and the methoxy acid finally liberated by acidification. It was repeatedly crystallised from dilute alcohol when it was obtained as colourless needles melting at 190°. [Found: C, 74·1; H, 5·9 per cent.; equivalent weight 242·9; $C_{15}H_{14}O_3$ requires C, 74·4 and H, 5·8 per cent.; equivalent weight 242·0.]

The same ether was obtained from the pyrone by the action of sodium methoxide and methyl iodide according to the method of Reychler.[11] But the yield and purity of the product were not good. However, it was more readily obtained from the pyrone by methylation with dimethyl sulphate and potash using aqueous methyl alcoholic medium. 4-Methyl-β-naphthopyrone (6 g.) was dissolved in a boiling mixture of methyl alcohol (50 c.c.) and 20 per cent. aqueous sodium hydroxide (50 c.c.). After cooling it to 50° the solution

was agitated with dimethyl sulphate (30 g.) which was slowly added in the course of half an hour. The reaction mixture was then made sufficiently alkaline, some more methyl iodide added and the whole boiled under reflux on a water-bath for three hours. The alcohol was then distilled off and the contents were diluted and acidified. The product was purified by solution in sodium bicarbonate and reprecipitation and crystallisation from dilute alcohol.

The methyl ether was unaffected by prolonged heating at its melting point. After treatment with mercuric oxide in both cold and hot alkaline solution it was recovered unchanged. Mercuric chloride in alcoholic or aqueous solution produced no change when boiled with the substance for two to three hours. After the heating was over, most of the alcohol was distilled off, a few drops of concentrated hydrochloric aicd added along with a large volume of water and the mixture allowed to cool. The original ether was recovered unchanged. A similar result was obtained by the action of mercuric acetate in neutral or faintly acid medium.

The methoxy acid was dissolved in anhydrous ethyl alcohol saturated with hydrogen chloride in the cold, allowed to stand for 24 hours and boiled under reflux for two hours. The alcohol was then distilled off, the residue treated with water and ether extracted. The oily liquid that was obtained from the ether solution on evaporation was hydrolysed with dilute alkali and the resulting acid isolated. It was identical with the original acid. The oil obtained during the course of the experiment was the ester of this acid.

β-1-Methoxy-2-naphthylcrotonic acid.—β-1-Hydroxy-2-naphthylcrotonic acid could not be obtained pure from 4-methyl-α-naphthopyrone. Though it was formed easily it underwent reversion into the pyrone readily on acidifying the alkaline solutions and the pyrone invariably contaminated it. The methoxy compound was, however, easily obtained by methylation of the pyrone with dimethyl sulphate in aqueous alcoholic potash. After three crystallisations from dilute alcohol it was obtained as colourless rectangular plates melting at 140°. [Found : C, 74·3 per cent. ; H, 5·3 per cent. ; $C_{15}H_{14}O_3$ requires C, 74·4 per cent. ; H, 5·8 per cent.]

The substance melted without decomposition. The action of mercuric compounds and alcoholic hydrogen chloride was studied carefully and they were found to produce no change, thus showing that it is not a *cis* compound.

β-2 : 4-Dimethoxyphenylcrotonic acid or methylether of 4-methoxy-β-methyl coumaric acid.—This was obtained from a number of starting materials using suitable methods as given below :—

(1) From β-2 : 4-dihydroxyphenylcrotonic acid (β-methylumbellic acid) by methylation with dimethyl sulphate in aqueous alkaline solution.

(2) From β-2-hydroxy-4-methoxyphenylcrotonic acid (β-methylumbellic acid methylether) by the same method.

(3) From 4-methyl-7-hydroxycoumarin by methylation with dimethyl sulphate in aqueous alcoholic solution.

(4) From 4-methyl-7-methoxycoumarin by using the same method.

All the samples were found to be identical. The substance crystallised from dilute alcohol as colourless needles melting at 150°. [Found : C, 65·0 ; H, 6·1 per cent. ; $C_{12}H_{14}O_4$ requires C, 64·9 ; H, 6·3 per cent.] This methoxy acid also melted without decomposition and was unaffected by all the reagents which produce *cis* to *trans* inversion.

β-2-Methoxy-4-methylphenylcrotonic acid or β-4-dimethylcoumaric acid methyl ether.—β : 4-Dimethylcoumaric acid was methylated using dimethyl sulphate and potash in aqueous solution. The ether so obtained crystallised from aqueous alcohol in the form of fibrous needles melting at 125-26°. [Found : C, 69·9 ; H, 7·0 ; OCH_3, 14·7 per cent. ; $C_{12}H_{14}O_3$ requires C, 69·9 ; H, 6·8 and OCH_3, 15·0 per cent.]

This substance exhibited the same behaviour as the other ethers described before and remained unchanged under conditions which bring about *cis* to *trans* inversion.

Summary.

The action of alkali on a number of coumarins with methyl groups in the 4-position has been studied in detail. Each of them yields readily only one acid which, though fairly stable, has the property of undergoing change into the corresponding coumarin under the action of heat and dehydrating agents. The acids, however, cannot be converted into stabler isomers by methods which are definitely effective in converting *cis* into *trans* acids. The methyl ethers of the acids are easily obtained by methylating the acids or the original pyrones in the presence of alkali in an aqueous alcoholic medium. Their properties are those of ethers of the *trans* acids since they cannot be converted into isomeric compounds by methods which are definitely successful in converting *cis* into *trans* ethers. It is therefore concluded that the acids and their ethers derived from 4-methylcoumarins are *trans* compounds. The comparatively ready formation of these acids and their ready conversion again into the coumarins are explained on the basis of the tautomeric mechanism which renders the geometrical inversion very facile.

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ON THE EMISSION SPECTRUM OF CCl_4.*

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The spectrum of the uncondensed discharge through flowing vapour of CCl_4 has been studied by Jevons.[1] In addition to the bands attributable to C_2 and CO, a prominent cluster of four bands was found in the ultra-voilet. Continuous emission bands were observed but have not been recorded † We have photographed the spectrum of an uncondensed discharge from a 1·5 K.W. transformer delivering 50,000 volts through flowing CCl_4 vapour, pressure being maintained constant between 0·2 and 0·3 mm. of Hg. Medium Hilger quartz spectrograph has been used to photograph the spectrum in the ultra-voilet region. The plates have been measured on the Abbe comparator using Cu arc lines as standards. The wave-lengths of the beginning, maximum and end of the continuous emission bands have been determined from microphotometer records, which were obtained on a Zeiss recording microphotometer. This shows continuous emission bands, the wave-lengths of whose maxima are approximately at λλ 4600, 3348, 3070, 2580, 2430, and (2345 ?). The full data on these continuous bands are given in Table I, and the accompanying microphotometer curve given in Fig. 1 shows the details. There was no trace of bands due to C_2.

Table I.

Long wave-length limit A.U.	Maxima A.U.	Short wave-length limit A.U.
5850	4600	4000
4000	3348	3260
3260	3070	3000
2700	2580	2500
2500	2430	2380
2380	2300 ?	2250

* A preliminary note has been published in *Curr. Sci.*, 1937, **5**, 474, which also contains a reproduction of the bands.

† Private communication from Dr. Jevons.

Among the CO bands the plate showed only a faint trace of the 0–0 band of the third positive carbon system. In addition to the continuous bands, the most characteristic feature of the spectrum was a prominent group of strong bands between λλ 2796 and 2777. Six heads could be distinguished of which four can be identified with bands observed by Jevons.[1] In addition to this group of bands the plate showed two more groups of weaker bands on either side of this region. All these bands are degraded towards shorter waves. The strong group of bands lies exactly in the region of the 0–1 bands of the 5B system of CO, but we have satisfied ourselves that it is different from 5B bands by obtaining direct spectrograms of CO. The differences in wave-lengths though slight, are outside the errors of observation and are confirmed by independent measurements of Jevons. Furthermore, the CCl_4 plates do not show any trace of the 0–0 band of 5B system which is about the same intensity as, if not slightly stronger than, the 0–1 band. Again the group of bands at λ 2846 which fortunately lies in the region free from CO bands definitely shows that the strong group also does not belong to CO. The accepted values of wave-lengths represent the mean of three measurements which agreed to within 0·2 A.U.

In Table II are listed the wave-lengths of the band heads observed here. Column 3 gives the wave-lengths as measured by Jevons.[1] The figures in brackets in each case represent visually estimated intensities. Column 4 contains the wave-lengths as recently measured on a heavily exposed plate by Dr. Jevons who has kindly communicated the results to one of us (R. K. A.).

In appearance these bands resemble very much the group of bands observed in the spectrum of the vapour of $SiCl_4$,[2] between λλ 2830 and 2770, and whose emitter is not yet definitely established. Some of the bands have a sharp line-like head as in these latter bands and show no indication of resolution. It is possible, however, to arrange them in the usual v', v'' table (Table III). The band at λ 2724·3 coincides with a mercury line and was, therefore, omitted in the preliminary publication. In view of the fact, however, that the resonance line of Hg at λ 2536·7 is not present on the plates, this is regarded as a band belonging to the system described. The only band not shown in the analysis is that at λ 2786·5 which, however, will probably fit into the scheme as one of the (2–2) bands. It may be mentioned that the band at λ 2782·4 coincides with a chlorine line.

The analysis as displayed in Table III indicates that the bands are due to a diatomic molecule. Apparently the CCl molecule suggests itself as the emitter.

TABLE II.

Authors λ A.U.	Int.	Jevons	
		Earlier Measurements λ A.U.	New Measurements λ A.U.
2862·0	(0)	..	..
2857·0	(4)	..	2856·83
2849·4	(4)	..	..
2846·0	(4)	..	2845·84
2795·9	(6)	..	..
*2789·5	(8)	..	2789·85
*2788·3	(8)	2788·2 (4)	2788·32
2786·5	(5)	..	2786·68
*2782·4	(8)	2782·3 (2)	2782·27
*2778·9	(6)	2778·6 (1)	2778·71
*2777·7	(8)	2777·5 (4)	2777·59
*2724·3	(0)	..	..
2713·4	(0)	..	..

* Sharp line-like heads, or strong line superposed on head.

TABLE III.

v' \ v''	0		1	
	λ Air A.U.	ν Vac. cm.$^{-1}$	λ Air A.U.	ν Vac. cm.$^{-1}$
	2795·9 (6) 35756	826	2862·0 (0) 34930	
	2789·5 (8) 35838	846	2857·0 (4) 34992	
0	2782·4 (8) 35930 137	845	2849·4 (4) 35085 135	
	2778·9 (6) 35975	848	2846·0 (4) 35127	
$\Delta\nu$	858, 868		862, 863	
	.....		.....	
	2724·3 (0) 36696	842	2788·3 (8) 35854	
1	 147		 136	
	2713·4 (0) 36843	853	2777·7 (8) 35990	

In Table IV are collected the data of the ground states of the known isoelectronic molecules formed by the atoms of the two short periods. It will

TABLE IV.

Molecule	No. of Electrons	Ground Term	$\Delta\nu_e$	ω_e''	$\omega_e'' x_e''$
CP	21	$^2\Sigma$	..	1239·67	6·86
SiN	21	$^2\Sigma$	..	1151·68	6·56
BeCl	21	$^2\Sigma$?	..	846·6	5·11
MgF	21	$^2\Sigma$	..	690·75	3·95
CS	22	$^1\Sigma$	..	1285·1	6·5
SiO	22	$^2\Sigma$	..	1242·0	6·05
NS	23	$^2\Pi$	223	1220·0	7·75
PO	23	$^2\Pi$	224	1230·6	6·52

Data from Sponer's *Molekuel Spektren*, Berlin, 1936.

be seer that a close correspondence exists between the various constants in each pair of molecules. The data for BeCl are not definite to establish the term taken here as the ground state of the molecule. The discrepancy may be due to the possibility that this level may not really be the ground state of the BeCl molecule.

If the emitter of the bands is taken as CCl, we obtain the following correspondence (Table V) between the constants of this molecule and that of the

TABLE V.

Molecule	Ground State	$\Delta\nu_e$	ω_e	$\omega_e''x_e''$
CCl ..	$^2\Pi$	136	843·6	?
SiF[4] ..	$^2\Pi$	161	844·7	4·7

iso-electronic molecule SiF. It may also be pointed out, as suggested by Dr. Jevons (private communication), that the constants here obtained fit very well as an extension to CCl, of the tables of constants given by Bashford, Briscoe and Jevons[3] for the fluorides, chlorides and bromides of Si, Ge, Sn, and Pb.‡

If this is true, the bands are the analogues of the β-bands of the SiF system, which have been shown to be due the transition B $^2\Sigma \rightarrow$ X $^2\Pi$. The excitation energy of the CCl band system is 4·4 e. volts and this also agrees with 4·29 e. volts, the excitation potential of the β-bands of SiF.[4] The only constant which does not completely agree is the electronic doublet separation $\Delta\nu_e$ of the ground state which is 136 cm.$^{-1}$ for CCl and 161·1 cm.$^{-1}$ for SiF. The difference between the frequencies of vibrations in the initial and final states being small, the transitions in which Δv is large are not expected. The conditions are favourable for the development of long sequences which, however, are not observed. Evidently, it has not been possible to derive the vibrational functions. The electronic structure of the molecule in the two states is expected to be similar to that of SiF, but unless more data are made available, this statement cannot be put to test.

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4. R. K. Asundi and R. Samuel, *Proc. Ind. Acad. Sci.*, 1936, **3**, 346.

‡ This is since shown in a paper by W. Jevons and L. A. Bashford, *Proc. Phys. Soc. Lond.*, 1937, **49**, 554.

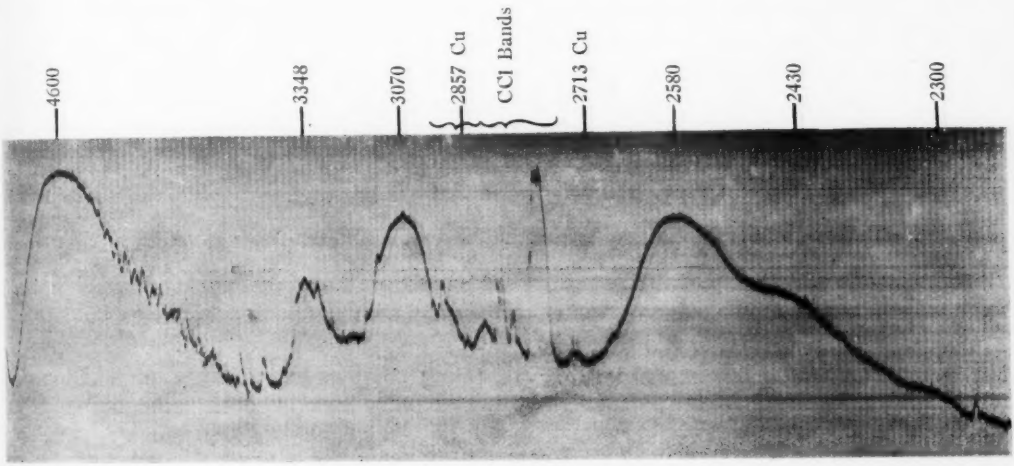

FIG. 1.

DIFFRACTION OF LIGHT BY RIPPLES ON LIQUID SURFACES—PART I.

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Received December 8, 1937.

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction.

As is well known the surface tension of liquids may be determined by the observation of ripples, the determination being based on the measurement of the wave-length λ* for some assigned frequency N of the ripple motion. The wave-length is determined by allowing a beam of light to be reflected or transmitted by the surface of the liquid and observing the distance between the successive maxima or minima of intensity in the reflected or transmitted beam. In the case of progressive waves, this is only possible by using intermittent light of the same frequency as the ripple motion. An alternative way of determining the wave-length is by the diffraction method. As was shown by Kalähne (1902) and more recently by Brown (1935) the ripples on a liquid surface act in the manner of a diffraction grating on a beam of light. Light from a collimator is allowed to fall on a liquid surface and the reflected beam is brought to a focus by means of a lens. This gives an image of the slit of the collimator on a screen placed at the focal point of the lens. When ripples are produced on the surface of the liquid, spectra are seen on either side of the original image on the screen. By measuring the separation between two successive orders, Kalähne calculated the wave-length of ripples. However, neither of these authors has considered the important question of the distribution of intensity in the diffraction spectra, as determined by the amplitude of the ripples. Actually the diffraction method can be used very effectively for studying both stationary and progressive wave-motion on liquid surfaces and has the advantage of not requiring the use of intermittent illumination. Further, the observation of the diffraction spectra is most conveniently made on a photograph taken with a relatively short exposure, and thus avoids the inconvenience of making protracted observations or counts of the ripples on the liquid surface visually. The diffraction spectra would be more widely separated the closer the ripples are, and hence the method is specially advantageous in working with ripples of high frequency. Very accurate measurements can be made of the distance between the successive 'ers of

the spectra with the result that the wave-length of the ripples can be determined with a high degree of precision. If the frequency of the ripples is known exactly, the surface tension can be calculated with a high degree of accuracy. Again, as the amplitude of the ripples can be calculated from the distribution of intensity in the diffraction spectra, it follows that in the case of progressive waves the damping can be estimated by taking photographs at various points along the direction of propagation of the ripples. The diffraction method also lends itself to the study of the damping of ripples by contaminated surfaces.

2. Theory of Diffraction of Light by Ripples.

Let the direction of propagation of the ripples be along the X-axis. If a parallel beam of light is made to fall on the surface, part of it is reflected and the other part transmitted. If the surface had been quite plane, then the wave-fronts of both the reflected and the transmitted beams of light would be plane. But on account of the ripples the surface behaves like a grating and hence the two wave-fronts are no longer plane but corrugated. The problem of reflection in such a case has been worked out by Lord Rayleigh (1896) in detail. Considering the case of transmission, it is easy to show, that, if the electric vector of the lightwave incident normally on the surface is represented by

$$Ae^{2\pi i\nu t}$$

it will be

$$Be^{2\pi i\nu\left\{t-\frac{(\mu-1)\,a\,(x)}{c}\right\}},$$

where it leaves the surface. Here μ is the refractive index of the liquid and $a\,(x)$ is the amplitude of the ripples at a distance x from the origin. We can put

$$a\,(x) = a \sin \frac{2\pi}{\lambda^*} x,$$

where a is the maximum value of the amplitude.

The electric vector due to the corrugated lightwave at a point, on a distant screen parallel to the surface of the liquid, whose join with the origin has its x direction cosine l, depends upon the evaluation of the diffraction integral

$$\int_{-p/2}^{p/2} e^{2\pi i\{lx + (\mu-1)\, a \sin(2\pi x/\lambda^*)\}/\lambda}\, dx,$$

where p is the length of the beam along the X-axis. This integral has been considered by Raman and Nath (1935) in their paper on the " Diffraction of Light by High Frequency Sound Waves ". Following their method, we get, if θ is the angle of diffraction corresponding to the nth order spectrum

$$\lambda^* \sin\theta = \pm n\lambda \qquad (1)$$

The intensity I_m of the mth order spectrum relative to I_n that of the nth order is given by

$$\frac{I_m}{I_n} = \frac{J_m^2(v)}{J_n^2(v)} \text{ where } v = \frac{2\pi(\mu - 1)a}{\lambda} \tag{2}$$

and J_m and J_n are Bessel functions of the mth order and the nth order respectively. The distribution of intensity amongst the various orders depends upon 'v' *i.e.*, upon the amplitude 'a'. Thus by a knowledge of the relative intensities of the various orders in the diffraction spectrum, the amplitude 'a' of the ripples can be determined. If a_0 is the amplitude of the ripples at the source and a_1 and a_2 the amplitudes at two points x_1 and x_2, we have, assuming an exponential law of decay,

$$a_1 = a_0 e^{-\alpha x_1}$$

$$\text{and} \quad a_2 = a_0 e^{-\alpha x_2}$$

$$\text{or} \quad a_1/a_2 = e^{\alpha(x_2 - x_1)}$$

$$\text{or} \quad \frac{v_1}{v_2} = e^{\alpha(x_2 - x_1)} \tag{3}$$

from which we can calculate α the damping coefficient if we know v_1 and v_2 at x_1 and x_2.

This value of α may be compared with that obtained from theory. Lamb (1924) has discussed the effect of the viscosity η of the liquid on the propagation of surface ripples and from the expressions he has derived it is easy to show that the damping coefficient

$$\alpha = \frac{4\pi\eta}{S} N \tag{4}$$

where S is the surface tension of the liquid. This shows that the damping coefficient varies directly as the frequency of the ripple motion or that $\frac{\alpha}{N}$ is a constant.

3. *Experimental.*

The apparatus employed is shown in Fig. I. T is a brass trough containing water. Light from a mercury vapour lamp M.L. is condensed on to a slit S. The lens L_2 renders this beam parallel which then is deflected through a right angle by the prism P_1. The light now passes through W, a window of good optical glass attached to a hole at the bottom of the trough. It is then turned through a right angle by means of the prism P_2 and brought to a focus by means of the lens L_3. At the focal point of L_3 is placed a photographic plate P.P. It will be noted that the rippled surface, instead of being used as a reflection grating as was done by Kalähne and Brown, is

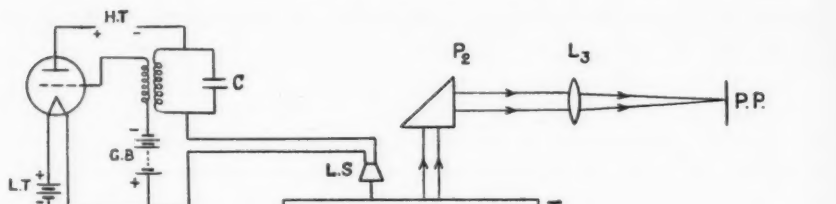

FIG. I.

used here as a transmission grating on account of the obvious reason that in the latter case considerable intensity of light is secured.

Ripples of various frequencies are produced on the surface by means of a dipper (which is the reed of a loudspeaker) actuated by means of a valve-circuit shown at the left in the figure. The dipper being a vertical line so to speak generates circular ripples on the surface of the liquid. By attaching a horizontal plate to the reed at its dipping end, straight ripples are produced. Both the dipper and the window are kept at sufficiently great distances from the sides of the trough so as to avoid complications arising from reflections. When water is used, it is necessary, in order to keep the surface clean and fresh, to sweep it by means of glass barriers coated with paraffin.

The loudspeaker unit is supported on a stand made in such a way that it can be moved vertically and also parallel to the length of the trough. The horizontal displacement of the reed relative to the glass window of the trough is measured by means of a scale.

In the neighbourhood of the dipper, the liquid surface is curved on account of capillarity. If this portion of the surface is in the path of the beam of light, errors are likely to arise. In order to avoid this, the dipper is always kept at a good distance from the point of observation.

4. Results and Discussion.

Photographs of the diffraction spectra have been given at the end of the paper. In Figs. II and III (Plate XIII) are shown the patterns obtained with straight ripples using frequencies 600 and 1150 respectively. Monochromatic light ($\lambda = 5461$ Å.U.) was employed. The wave-lengths were calculated

from equation (1) and the surface tension from the well-known relation

$$N^2 \lambda^{*2} = V^2 = \frac{\lambda^*}{2\pi}\left(g + \frac{4\pi^2 S}{\lambda^{*2}\rho}\right),$$

where ρ is the density of the liquid, g is the gravity and V is the velocity of the ripples. The values of the surface tensions obtained were between 71 and 76. Under the conditions of the experiment it is believed that this must be attributed to the small errors in the values of the frequencies. Photographs of the diffraction spectra given by circular ripples were also taken but they were not very well defined. The pictures in Figs. II and III show the change in the diffraction pattern due to the decrease in the amplitude of the ripples caused by removing the vibrator away from the point of observation. Similar effects are also obtained when the dipper is kept at the same point and its amplitude varied. The distribution of intensity in the spectra is given by the expressions in (2). Raman and Nath, in their paper, have discussed the variation of the ratio $\frac{J_m^2(v)}{J_n^2(v)}$ as a function of v and have given diagrams (reproduced in Fig. VI) showing the intensity distribution in the diffraction pattern with increasing values of v. The

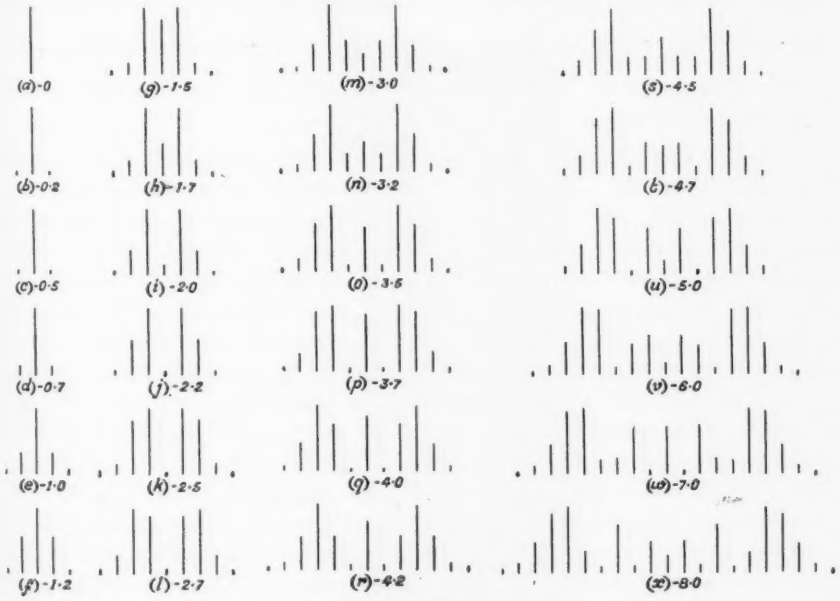

FIG. VI.

Relative intensities of the various components in the diffraction spectra.

number of orders increases as v increases. When $v = 0$ we have only the central component. As v increases from zero the first orders on either side begin to appear. As v increases still more the first orders become more intense in relation to the central order and the second orders begin to appear. With further increase in v the central order goes on diminishing in intensity until it almost disappears, while the first and the second orders go on steadily increasing in intensity and the third orders make their appearance and grow in intensity. For still greater values of v the central order is reborn and increases in intensity whereas the first orders go on diminishing; the second and the third orders brighten further and the fourth order just makes its appearance, and so on. The pictures given illustrate the wandering of the intensity amongst the various orders. The same effect is shown markedly by the microphotometer curves for the pictures in Fig. III given in Fig. V (Plate XIV). The amplitudes corresponding to the patterns in Fig. V are $7 \cdot 8 \times 10^{-5}$ cm., $4 \cdot 0 \times 10^{-5}$ cm. and $2 \cdot 9 \times 10^{-5}$ cm. respectively. The damping coefficients for the two frequencies 600 and 1150 are found to be 1·29 and 1·9 respectively giving $\frac{a}{N} = \cdot 00215$ and $\cdot 00165$. The value of $\frac{a}{N}$ calculated from theory, *i.e.*, equation (4) is $\cdot 00172$. Considering the fact that the frequencies were not known quite exactly, the values of $\frac{a}{N}$ obtained from the experiment must be regarded as being in agreement with the value obtained from theoretical considerations.

As has been shown by Pockels (1891), ripples are also damped by the presence on the surface of a mono-molecular film of oil insufficient to cover the whole surface; the extent of damping increases with an increasing proportion of the surface covered until the whole is covered. Gorter and Seeder (1932) made the first measurements of the amplitudes of stationary ripples by causing a beam of parallel light to fall normally on a rippled surface and observing the maximum angle between the reflected rays. Measurements were taken when thin films were present on the surface and a decrease of amplitude was observed when the films were compressed. Using this method, Sameshima and Sasaki (1936) have made studies of mono-molecular films on the surface of water. Fig. IV (Plate XIII) shows the results obtained by employing the diffraction method for the study of this phenomenon. The picture at the top in Fig. IV was the one obtained with a fresh uncontaminated water surface. A small quantity of palmitic acid ($\cdot 4 \times 10^{-4}$ gm.) was then spread on the surface and photographs of the diffraction pattern were taken at various stages as the film was compressed. The continuous increase in the damping is strikingly shown by the pictures.

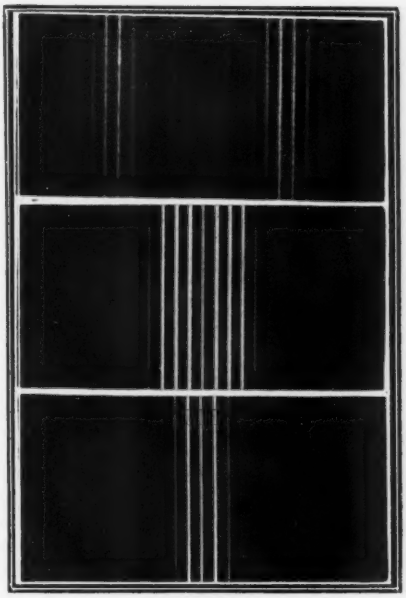

FIG. II.

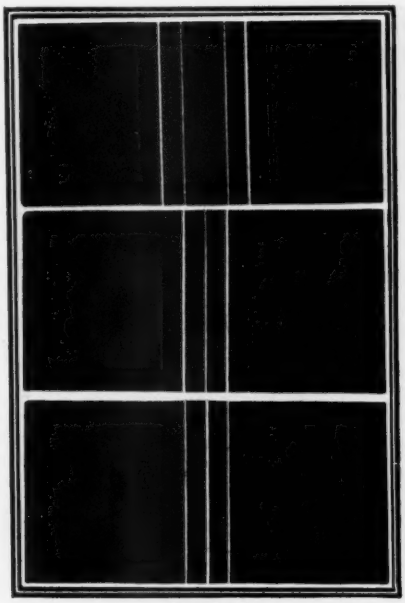

FIG. III.

FIG. IV.

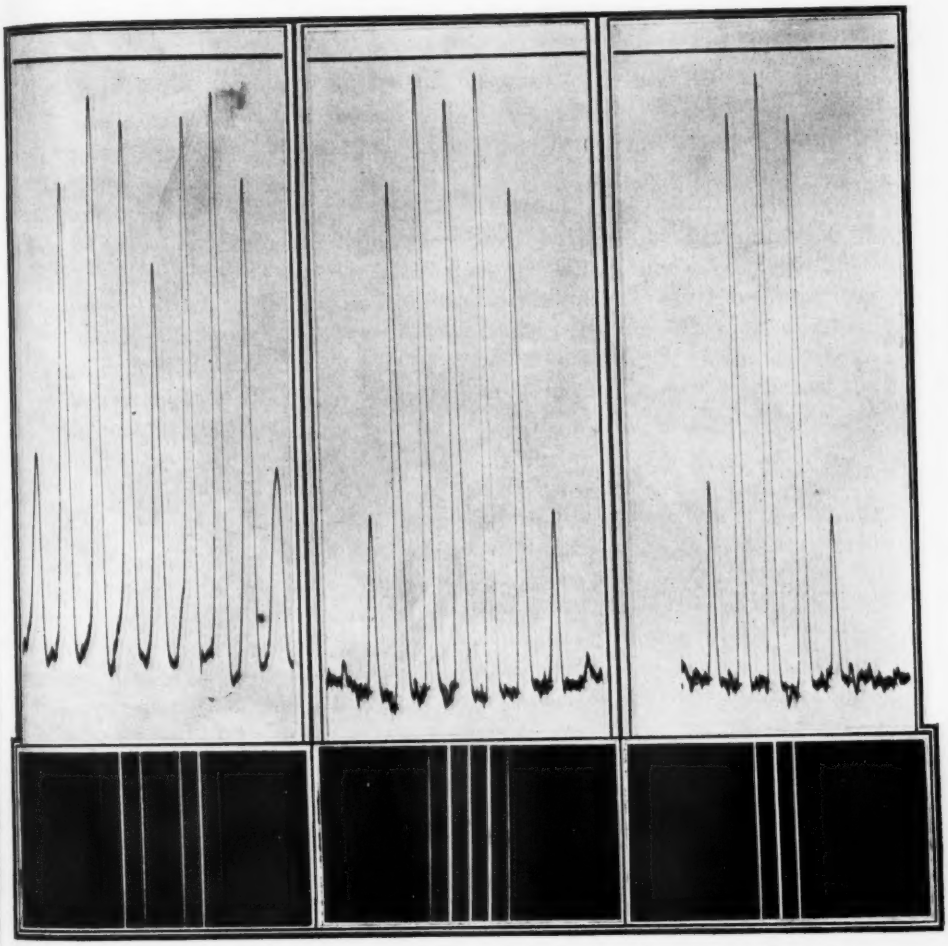

FIG. V.

It is found that the ratio of the amplitude of the damped wave to that of the undamped one is approximately proportional to the area of the surface covered by the film. However, accurate measurements are necessary before any quantitative estimates can be made and the pictures given only serve to show the applicability of the method.

In conclusion, it is my pleasant duty to express my heartfelt thanks to my professor, Sir C. V. Raman, for his kind encouragement and inspiring guidance.

5. *Summary.*

Using monochromatic light, the spectra obtained by the diffraction of light by a system of ripples travelling on a liquid surface have been photographed. The distribution of intensity in the spectra is a function of the amplitude of the ripples, the problem being similar to the one discussed by Raman and Nath in their paper entitled "Diffraction of Light by High Frequency Sound Waves". The ratio of the intensities of the mth and the nth order is given by

$$\frac{J_m^2(v)}{J_n^2(v)}, \quad \text{where } v = \frac{2\pi\,(\mu - 1)}{\lambda}\, a,$$

where a is the amplitude of the ripples, μ the refractive index of the liquid, λ the wave-length of the monochromatic light used, and J_m and J_n are Bessel functions of the mth and the nth order respectively. It is shown that by employing the diffraction method, a quantitative study can be made of the damping of progressive ripples on the surface by taking photographs at some points along the direction of propagation of the ripples and also of the damping of ripples due to surface contaminations, in this case the photographs being taken as the film is compressed. Some calculations have also been given.

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STUDIES ON THE DEPENDENCE OF OPTICAL ROTATORY POWER ON CHEMICAL CONSTITUTION.

Part XV. Chloroaryl Derivatives of Stereoisomeric Methylenecamphors.

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and
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Received November 29, 1937.

The object of the paper was to study the effect of substitution of the hydrogen atom by chlorine on the rotatory dispersion of anilinomethylenecamphor. We have, therefore, condensed chloranilines (*o*, *m*, *p*), *2 : 4*-dichloranilines and *2 : 4 : 6*-trichloranilines with oxymethylenecamphor (*d*, *l*, *dl*).

Effect of Chemical Constitution on the Rotatory Power.—The replacement of a hydrogen atom in benzene nucleus by a negative group such as chlorine tends to decrease the electrostatic moment.[1] If it is supposed that there is any relation between electrostatic moment of a compound and its rotatory power, we shall expect that these properties will be affected alike ; a decrease in the electrostatic moment of the compound should result in the decrease of its rotatory power. The experimental results now recorded bear this out. The rotatory power of monochloro-derivatives of anilinomethylenecamphors are lower than those of the parent compound in all the six solvents examined and for all wave-lengths, from $\lambda = 4800$ Å.U. to 6708 Å.U.

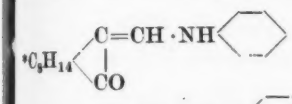
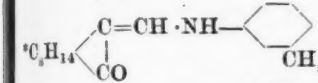
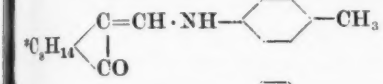
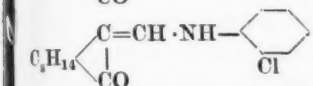
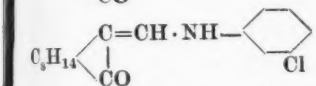
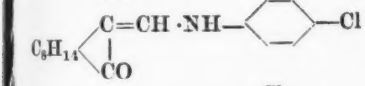
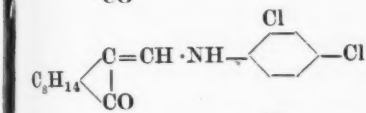
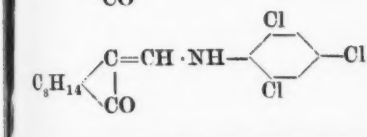
This is further confirmed by the observations with *2 : 4*-dichloro and *2 : 4 : 6*-trichloro derivatives of anilinomethylenecamphors which show progressive diminution in the rotatory power (see Table A).

The chlorophenyl derivatives of aminomethylenecamphors have lower rotatory power than the toluidinomethylenecamphors and the latter have lower rotatory power than that of anilinomethylenecamphors.[2] The sequence of the different substituent groups in the series is, therefore, $H > CH_3 > Cl$ which agrees with the polar series deduced from electronic theory.

Influence of Substituents on Rotatory Power of the Position Isomerides.—The sequence of the rotatory power of the position isomerides (Table A) is *un* > *p* > *o* > *m* in methyl alcohol, ethyl alcohol and pyridine ;

[1] Thomson, *Phil. Mag.*, **46**, 497.
[2] Singh, Bhaduri and Barat, *J. Ind. Chem. Soc.*, 1931, **8**, 345.

TABLE A.

Structural formulæ	$[\alpha]^{35°}_{Hg\,gr}$					
	MeOH	EtOH	Acetone	Pyridine	Chloro-form	Benzene
	480·0°	451·3°	448·9°	433.2°	424·6°	367·1°
	454·4	439·9	442·3	405·8	384·8	362·6
	465·0	440·8	425·8	401·6	401·6	355·4
	400·2	405·8	380·0	391·3	386·0	364·7
	388·5	384·7	388·0	374·4	381·4	363·6
	417·7	406·3	401·8	394·4	374·6	359·4
	362·5	369·3	362·3	367·9	366·6	337·9
	259·8	265·2	258·7	250·8	255·0	219·1

* Singh, Bhaduri and Barat, *loc. cit.*

un > *o* > *m* > *p* in chloroform and benzene and *un* > *p* > *m* > *o* in acetone. This is neither in agreement with Frankland's lever arm hypothesis[3] nor with the electrostatic modification as suggested by Rule,[4] as the *unsubstituted* compound has always the highest rotatory power in all these cases. This point has already been emphasised in previous communications.[5]

[3] *J. Chem. Soc.*, 1896, **69**, 1583.

[4] *J. Chem. Soc.*, 1924, **125**, 1122.

[5] Singh, Mallik and Bhaduri, *J. Ind. Chem. Soc.*, 1931, **8**, 95; Singh, Bhaduri and Barat, *loc. cit.*

Nature of Solvents and the Rotatory Power.—The compounds studied in the present paper have, in general, highest rotations in alcohol (ethyl and methyl) and lowest as a rule, in benzene. For other solvents no fixed sequence is observed. This is in agreement with the sequence of the dielectric constants of the solvents; the positions of chloroform, acetone and pyridine are however frequently interchanged (*vide* Tables I–XXX).

The Nature of Rotatory Dispersion.—The rotatory dispersion is found, as with the other compounds of the series,[6] to obey the simple dispersion law, $[\alpha] = \frac{k}{\lambda^2 - \lambda_0^2}$. In the numerical test given in the tables of rotatory dispersion (I–XXX), this point is clearly brought out as the differences in the observed and calculated values of rotatory power lie well within the range of experimental error.

Physical Identity of Isomers.—The values of rotatory power of *d* and *l* forms in different solvents (Tables I–XXX) are identical within limits of experimental errors. Out of 258 observations now recorded, in as many as 231 cases the difference in the numerical value of specific rotatory power of the opposite isomers corresponds to a difference of less than 0·01° in the observed angle of rotation and in 23 other cases the corresponding angle lies between 0·01°–0·02° which is the limit of experimental error allowable in such measurements. Only in the remaining 4 cases, *viz.*, *m*-chloranilinomethylenecamphor in acetone for Ag_{5209} (Table IX) and in pyridine for Cd_{5086} (Table X); *2 : 4*-dichloranilinomethylenecamphor in ethyl alcohol for Cd_{4800} (Table XXIII); and *2 : 4 : 6*-trichloranilinomethylenecamphor in methyl alcohol (Table XXX) the difference corresponds to between 0·02° and 0·03° in the observed angle of rotation. All these are, however, of the nature of casual experimental errors. This therefore further supports Pasteur's principle of molecular dissymmetry, according to which the two forms, *dextro* and *lævo*, must possess equal and opposite rotatory power.

The melting point of the *racemic* form of *2 : 4*-dichloranilinomethylenecamphor is higher than those of the optically active forms. This form is a true *dl* compound, at least in the solid state.

Experimental.

General Method of Preparation.—The solution of the free base (1 mol. proportion) in *glacial* acetic acid is added to a solution of *oxymethylene*-d-*camphor* (1 mol. proportion) in methyl alcohol, when a precipitate usually

[6] Singh and Bhaduri, *J. Ind. Chem. Soc.*, 1930, **7**, 771; 1931, **8**, 181; Singh, Bhaduri and Barat, *loc. cit.*

separates at once ; if not, it is left overnight to crystallise slowly (*without* any addition of water). It is then repeatedly crystallised out of suitable solvents, usually methyl alcohol.

The *lævo* and the *racemic* compounds described in the present paper were prepared in the same way as the corresponding *dextro* isomers and have the same crystalline form and similar solubility.

o-*Chloranilinomethylene*-d-*camphor*, faintly yellowish, almost white prismatic needles, m.p. 103°–04°. (Found : C, 70·28 ; H, 6·98 ; $C_{17}H_{20}ClON$ requires C, 70·45 ; H, 6·92 and N, 4·83 per cent.) It is very soluble in pyridine, chloroform, acetone and benzene ; less so in ethyl alcohol and methyl alcohol. The *l*-form, m.p. 103°–04°. (Found : N, 4·86). The *dl*-form m.p. 92°–93° (Found : N, 4·86).

m-*Chloranilinomethylene*-d-*camphor*, long rectangular white plates, m.p. 118°–19°. (Found : C, 70·32 ; H, 6·99 ; $C_{17}H_{20}ClON$ requires C, 70·45 ; H, 6·92 ; and N, 4·83 per cent.) It is very easily soluble in chloroform, pyridine, acetone and benzene ; difficultly in ethyl alcohol and methyl alcohol. The *l*-form, m.p. 118°–19°. (Found : N, 4·96). The *dl*-form m.p. 114°–15°. (Found : N, 4·87).

p-*Chloranilinomethylene*-d-*camphor*, shining long rectangular white plates, m.p. 186°–87°. (Found : C, 70·32 ; H, 7·26 ; $C_{17}H_{20}ClON$ requires C, 70·45 ; H, 6·92 and N, 4·83 per cent.) It is very easily soluble in chloroform, acetone and pyridine ; less so in ethyl alcohol and methyl alcohol ; and difficultly soluble in benzene and ether. The *l*-form, m.p. 186°–87°. (Found : N, 4·84). The *dl*-form, m.p. 185°–87°. (Found : N, 4·96).

2 : 4. *Dichloranilinomethylene*-d-*camphor*, long white silky needles, m.p. 122°–23°. (Found : C, 62·90 ; H, 6·01 ; $C_{17}H_{19}Cl_2NO$ requires C, 62·98 ; H, 5·86 and N, 4·32 per cent.) It is very easily soluble in chloroform, acetone, pyridine, benzene, and ethyl alcohol ; less so in methyl alcohol. The *l*-form m.p., 122°–23°. (Found : N, 4·36). The *dl*-form m.p., 126°–27°. (Found : N, 4·36).

2 : 4 : 6. *Trichloranilinomethylene*-d-*camphor*, shining white prismatic needles, m.p. 108°-09°. (Found : C, 56·78 ; H, 5·05 ; $C_{17}H_{18}Cl_3NO$ requires C, 56·90 ; H, 5·02 and N, 3·90 per cent.) It is very soluble in pyridine, chloroform, benzene and acetone ; less so in ethyl alcohol and methyl alcohol. The *l*-form, m.p. 108°-09°. (Found : N, 4·10). The *dl*-form, m.p. 107°-08°. (Found : N, 3·96).

The rotatory power determinations were made in a 2-dcm. jacketed tube at 35°. The value of λ_0, calculated from the dispersion formula, is given in the tables and is expressed as μ or 10^{-4} cm.

TABLE I. *c-Chloranilinomethylenecamphor in chloroform.*

$$[\alpha] = \pm \frac{61 \cdot 79}{\lambda^2 - 0 \cdot 1382}; \quad \lambda_0 = 0 \cdot 3717.$$

Dextro			Line	Calc. [α] *c*	*Lævo*		
Concentration g./100 c.c.	Obs. [α] *o*	*o–c*			*o′–c*	Obs. [α] *o′*	Concentration g./100 c.c.
0·4004	+669·4°	−0·8°	Cd_{4800}	±670·2°	−0·3°	−669·9°	0·4024
,,	513·2	+0·4	Cd_{5086}	512·8	+0·5	513·3	,,
,,	464·6	+0·5	Ag_{5209}	464·1	−0·6	463·5	,,
,,	386·0	−0·2	Hg_{5461}	386·2	+0·4	386·6	,,
,,	314·8	−0·7	Hg_{5780}	315·5	+0·1	315·6	,,
,,	294·7	−0·8	Na_{5893}	295·5	−0·9	294·6	,,
,,	264·7	+1·1	Li_{6104}	263·6	−0·1	263·5	,,
,,	223·6	−0·1	Cd_{6438}	223·7	+0·1	223·8	,,
,,	198·5	+0·3	Li_{6708}	198·2	+0·6	198·8	,,

The solution did not exhibit mutarotation.

TABLE II. *o-Chloranilinomethylenecamphor in pyridine.*

$$[\alpha] = \pm \frac{63 \cdot 72}{\lambda^2 - 0 \cdot 1352}; \quad \lambda_0 = 0 \cdot 3691.$$

Dextro			Line	Calc. [α] *c*	*Lævo*		
Concentration g./100 c.c.	Obs. [α] *o*	*o–c*			*o′–c*	Obs. [α] *o′*	Concentration g./100 c.c.
0·4000	+515·0°	−0·9°	Cd_{5086}	±515·9°	+0·2°	−516·1°	0·4040
,,	468·8	+0·6	Ag_{5209}	468·2	−0·5	467·7	,,
,,	391·3	+0·4	Hg_{5461}	390·9	+0·2	391·1	,,
,,	320·0	−0·4	Hg_{5780}	320·4	+0·2	320·6	,,
,,	301·3	+0·9	Na_{5893}	300·4	−0·9	299·5	,,
,,	268·8	+0·3	Li_{6104}	268·5	+0·1	268·6	,,
,,	227·5	−0·6	Cd_{6438}	228·1	−0·3	227·8	,,
,,	202·5	+0·1	Li_{6708}	202·4	−0·6	201·8	,,

The solution did not exhibit mutarotation.

TABLE III. o-*Chloranilinomethylenecamphor in benzene.*

$$[\alpha] = \pm \frac{57{\cdot}76}{\lambda^2 - 0{\cdot}1462}\ ;\ \lambda_0 = 0{\cdot}3824.$$

Dextro			Line	Calc. [α] *c*	*Lævo*		
Concentration g./100 c.c.	Obs. [α] *o*	*o–c*			*o′–c*	Obs. [α] *o′*	Concentration g./100 c.c
0·4004	+487·1°	−0·2°	Cd_{5086}	±487·3°	+0·1°	−487·4°	0·4032
,,	442·0	+1·4	Ag_{5209}	440·6	−0·2	440·4	,,
,,	364·7	−0·9	Hg_{5461}	365·6	+0·2	365·8	,,
,,	297·2	−0·7	Hg_{5780}	297·9	−0·3	297·6	,,
,,	279·7	+0·8	Na_{5893}	278·9	+0·1	279·0	,,
,,	248·5	±0	Li_{6104}	248·5	+0·8	249·3	,,
,,	211·0	+0·5	Cd_{6438}	210·5	−0·9	209·6	,,
,,	186·1	−0·3	Li_{6708}	186·4	+0·4	186·0	,,

The solution did not exhibit mutarotation.

TABLE IV. o-*Chloranilinomethylenecamphor in acetone.*

$$[\alpha] = \pm \frac{61{\cdot}42}{\lambda^2 - 0{\cdot}1368}\ ;\ \lambda_0 = 0{\cdot}3699.$$

Dextro			Line	Calc. [α] *c*	*Lævo*		
Concentration g./100 c.c.	Obs. [α] *o*	*o–c*			*o′–c*	Obs. [α] *o′*	Concentration g./100 c.c.
0·4000	+655·0°	−1·1°	Cd_{4800}	±656·1°	..	..	0·4020
,,	503·8	−0·1	Cd_{5086}	503·9	+0·4°	−504·3°	,,
,,	457·5	+0·9	Ag_{5209}	456·6	−0·8	455·8	,,
,,	380·0	−0·6	Hg_{5461}	380·6	+0·3	380·9	,,
,,	310·0	−1·3	Hg_{5780}	311·3	−0·1	311·2	,,
,,	292·5	+0·7	Na_{5893}	291·8	+0·8	292·6	,,
,,	260·0	−0·4	Li_{6104}	260·4	−0·1	260·3	,,
,,	221·3	+0·1	Cd_{6438}	221·2	+0·4	221·6	,,
,,	197·5	+1·4	Li_{6708}	196·1	−0·6	195·5	,,

The solution did not exhibit mutarotation.

TABLE V. o-*Chloranilinomethylenecamphor in methyl alcohol.*

$$[\alpha] = \pm \frac{64 \cdot 77}{\lambda^2 - 0 \cdot 1361}; \quad \lambda_0 = 0 \cdot 3689.$$

Dextro			Line	Calc. $[\alpha]$ c	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]$ o	$o-c$			$o'-c$	Obs. $[\alpha]$ o'	Concentration g./100 c.c.
0·4024	+687·2°	+0·3°	Cd_{4800}	±686·9°	+0·6°	−687·5°	0·4000
,,	526·9	−1·4	Cd_{5086}	528·3	−0·8	527·5	,,
,,	479·7	+0·7	Ag_{5209}	479·0	+1·0	480·0	,,
,,	400·2	+0·6	Hg_{5461}	399·6	+1·6	401·2	,,
,,	326·9	−0·2	Hg_{5780}	327·1	−0·8	326·3	,,
,,	308·2	+0·3	Na_{5893}	306·7	+0·8	307·5	,,
,,	273·3	−0·6	Li_{6104}	273·9	−0·1	273·8	,,
,,	233·6	+0·9	Cd_{6438}	232·7	−0·2	232·5	,,
,,	206·3	−0·1	Li_{6708}	206·4	+1·1	207·5	,,

The solution did not exhibit mutarotation.

TABLE VI. o-*Chloranilinomethylenecamphor in ethyl alcohol.*

$$[\alpha] = \pm \frac{72 \cdot 23}{\lambda^2 - 0 \cdot 1203}; \quad \lambda_0 = 0 \cdot 3468.$$

Dextro			Line	Calc. $[\alpha]$ c	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]$ o	$o-c$			$o'-c$	Obs. $[\alpha]$ o'	Concentration g./100 c.c.
0·4016	+654·9°	−1·1°	Cd_{4800}	±656·0°	−1·0°	−655·0°	0·4000
,,	522·9	+1·0	Cd_{5086}	521·9	+0·6	522·5	,,
,,	478·1	−0·2	Ag_{5209}	478·3	−0·8	477·5	,,
,,	405·8	−0·3	Hg_{5461}	406·1	+0·2	406·3	,,
,,	338·1	+0·3	Hg_{5780}	337·8	−0·3	337·5	,,
,,	318·7	+0·5	Na_{5893}	318·2	+0·6	318·8	,,
,,	286·3	±0	Li_{6104}	286·3	+1·2	287·5	,,
,,	245·2	−0·3	Cd_{6438}	245·5	−0·5	245·0	,,
,,	219·1	±0	Li_{6708}	219·1	−0·3	218·8	,,

The solution did not exhibit mutarotation.

TABLE VII. m-*Chloranilinomethylenecamphor in chloroform.*

$$[\alpha] = \pm \frac{61{\cdot}22}{\lambda^2 - 0{\cdot}1372}\,;\ \lambda_0 = 0{\cdot}3704.$$

Dextro			Line	Calc. $[\alpha]$ c	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]$ o	$o-c$			$o'-c$	Obs. $[\alpha]$ o'	Concentration g./100 c.c.
0·4024	+657·4°	+0·5°	Cd_{4800}	±656·9°	+1·2°	−568·1°	0·4020
,,	503·4	−0·5	Cd_{5086}	503·9	−1·3	502·6	,,
,,	456·1	−0·5	Ag_{5209}	456·6	±0	456·6	,,
,,	381·4	+1·1	Hg_{5461}	380·3	+0·4	380·7	,,
,,	311·8	+0·8	Hg_{5780}	311·0	±0	311·0	,,
,,	291·0	−0·4	Na_{5893}	291·4	−0·3	291·1	,,
,,	259·8	−0·3	Li_{6104}	260·1	−1·3	258·8	,,
,,	221·2	+0·4	Cd_{6438}	220·8	+0·3	221·1	,,
,,	195·2	−0·6	Li_{6708}	195·8	−0·6	195·2	,,

The solution did not exhibit mutarotation but turned light pink on keeping.

TABLE VIII. m-*Chloranilinomethylenecamphor in ethyl alcohol.*

$$[\alpha] = \pm \frac{62{\cdot}47}{\lambda^2 - 0{\cdot}1354}\,;\ \lambda_0 = 0{\cdot}3680.$$

Dextro			Line	Calc. $[\alpha]$ c	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]$ o	$o-c$			$o'-c$	Obs. $[\alpha]$ o'	Concentration g./100 c.c.
0·4028	+658·1°	+0·4°	Cd_{4800}	±657·7°	−0·2°	−657·5°	0·4000
,,	505·4	−1·2	Cd_{5086}	506·6	−1·1	505·1	,,
,,	459·3	−0·4	Ag_{5209}	459·7	+0·3	460·0	,,
,,	384·7	+1·0	Hg_{5461}	383·7	+0·1	383·8	,,
,,	315·2	+0·8	Hg_{5780}	314·4	+0·6	315·0	,,
,,	294·3	−0·5	Na_{5893}	294·8	−1·0	293·8	,,
,,	263·2	−0·2	Li_{6104}	263·4	+0·4	263·8	,,
,,	224·8	+1·0	Cd_{6438}	223·8	−1·3	222·5	,,
,,	198·6	±0	Li_{6708}	198·6	+0·2	198·8	,,

The solution did not exhibit mutarotation.

TABLE IX. m-*Chloranilinomethylenecamphor in acetone.*

$$[\alpha] = \pm \frac{63 \cdot 65}{\lambda^2 - 0 \cdot 1341}; \quad \lambda_0 = 0 \cdot 3662.$$

Dextro			Line	Calc. $[\alpha]$ c	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]$ o	$o-c$			$o'-c$	Obs. $[\alpha]$ o'	Concentration g./100 c.c.
0·4008	+660·0°	−1·0°	Cd_{4800}	±661·0°	..	..	0·4040
,,	511·4	+0·7	Cd_{5086}	510·7	−0·8°	−509·9°	,,
,,	462·7	−1·2	Ag_{5209}	463·9	+1·3	465·2	,,
,,	388·0	+0·1	Hg_{5461}	387·9	−0·2	387·7	,,
,,	318·1	−0·2	Hg_{5780}	318·3	+0·9	319·2	,,
,,	298·2	−0·3	Na_{5893}	298·5	−0·2	298·3	,,
,,	266·9	±0	Li_{6104}	266·9	+0·4	267·3	,,
,,	227·0	±0	Cd_{6438}	227·0	−0·5	226·5	,,
,,	202·0	+0·5	Li_{6708}	201·5	+0·2	201·7	,,

The solution did not exhibit mutarotation.

TABLE X. m-*Chloranilinomethylenecamphor in pyridine.*

$$[\alpha] = \pm \frac{63 \cdot 70}{\lambda^2 - 0 \cdot 1275}; \quad \lambda_0 = 0 \cdot 3571.$$

Dextro			Line	Calc. $[\alpha]$ c	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]$ o	$o-c$			$o'-c$	Obs. $[\alpha]$ o'	Concentration g./100 c.c.
0·4020	+618·4°	−0·6°	Cd_{4800}	±619·0°	+1·1°	−620·1°	0·4040
,,	486·5	+1·0	Cd_{5086}	485·5	−1·5	484·0	,,
,,	442·7	−0·2	Ag_{5209}	442·9	−1·0	441·9	,,
,,	374·4	+1·2	Hg_{5461}	373·2	+0·5	373·7	,,
,,	308·5	+0·2	Hg_{5780}	308·3	−0·1	308·2	,,
,,	289·8	±0	Na_{5893}	289·8	+1·1	290·9	,,
,,	258·8	−1·0	Li_{6104}	259·8	−1·1	258·7	,,
,,	222·7	+0·8	Cd_{6438}	221·9	+0·9	222·8	,,
,,	196·6	−0·9	Li_{6708}	197·5	−0·7	196·8	,,

The solution did not exhibit mutarotation.

TABLE XI. m-*Chloranilinomethylenecamphor in methyl alcohol.*

$$[\alpha] = \pm \frac{63{\cdot}14}{\lambda^2 - 0{\cdot}1361}\,;\ \lambda_0 = 0{\cdot}3689.$$

Dextro			Line	Calc. $[\alpha]$ c	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]$ o	$o-c$			$o'-c$	Obs. $[\alpha]$ o'	Concentration g./100 c.c.
0·4040	+670·9°	+1·3°	Cd_{4800}	±669·6°	..	..	0·4000
,,	516·1	+1·1	Cd_{5086}	515·0	+1·2°	−516·2°	,,
,,	466·6	−0·4	Ag_{5209}	467·0	−0·7	466·3	,,
,,	388·5	−1·0	Hg_{5461}	389·5	+0·5	390·0	,,
,,	319·3	+0·4	Hg_{5780}	318·9	−0·1	318·8	,,
,,	298·2	−0·8	Na_{5893}	299·0	−0·2	298·8	,,
,,	267·2	+0·2	Li_{6104}	267·0	+0·5	267·5	,,
,,	226·4	−0·4	Cd_{6438}	226·8	−0·5	226·3	,,
,,	200·6	−0·6	Li_{6708}	201·2	+0·1	201·3	,,

The solution did not exhibit mutarotation.

TABLE XII. m-*Chloranilinomethylenecamphor in benzene.*

$$[\alpha] = \pm \frac{60{\cdot}73}{\lambda^2 - 0{\cdot}1311}\,;\ \lambda_0 = 0{\cdot}3621.$$

Dextro			Line	Calc. $[\alpha]$ c	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]$ o	$o-c$			$o'-c$	Obs. $[\alpha]$ o'	Concentration g./100 c.c.
0·3988	+476·4°	+1·5°	Cd_{5086}	±474·9°	+1·4°	−476·3°	0·4000
,,	432·5	−0·7	Ag_{5209}	433·2	−0·7	432·5	,,
,,	363·6	+0·2	Hg_{5461}	363·4	+0·4	363·8	,,
,,	299·6	+0·4	Hg_{5780}	299·2	−0·4	298·8	,,
,,	280·8	−0·1	Na_{5893}	280·9	+0·4	281·3	,,
,,	250·6	−0·9	Li_{6104}	251·5	−0·2	251·3	,,
,,	214·3	±0	Cd_{6438}	214·3	+0·7	215·0	,,
,,	190·5	±0	Li_{6708}	190·5	−0·5	190·0	,,

The solution did not exhibit mutarotation.

TABLE XIII. p-*Chloranilinomethylenecamphor in chloroform.*

$$[\alpha] = \pm \frac{67 \cdot 56}{\lambda^2 - 0 \cdot 1176}\ ;\ \lambda_0 = 0 \cdot 3429.$$

Dextro			Line	Calc. $[\alpha]$ c	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]$ o	$o-c$			$o'-c$	Obs. $[\alpha]$ o'	Concentration g./100 c.c.
0·4004	+598·1°	−0·9°	Cd_{4800}	±599·0°	..	..	0·4000
,,	479·5	+0·6	Cd_{5086}	478·9	+1·1°	−480·0°	,,
,,	439·5	−0·3	Ag_{5209}	439·8	+1·1	440·0	,,
,,	374·6	+0·5	Hg_{5461}	374·1	−0·3	373·8	,,
,,	312·2	+0·2	Hg_{5780}	312·0	+0·5	312·5	,,
,,	293·6	−0·5	Na_{5893}	294·1	−0·3	293·8	,,
,,	266·0	+1·0	Li_{6104}	265·0	±0	265·0	,,
,,	227·3	−0·3	Cd_{6438}	227·6	+1·2	228·8	,,
,,	202·3	−0·9	Li_{6708}	203·2	−0·7	202·5	,,

The solution exhibited slight mutarotation ; the initial values $[\alpha]_{Hg_{gr}} = 374 \cdot 6°$ and $[\alpha]_{Hg_y} = 312 \cdot 2°$ changing to 363·4° and 303·5° respectively in course of 18 hours, the solution turning light yellow on keeping.

TABLE XIV. p-*Chloranilinomethylenecamphor in benzene.*

$$[\alpha] = \pm \frac{57 \cdot 80}{\lambda^2 - 0 \cdot 1375}\ ;\ \lambda_0 = 0 \cdot 3708.$$

Dextro			Line	Calc. $[\alpha]$ c	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]$ o	$o-c$			$o'-c$	Obs. $[\alpha]$ o'	Concentration g./100 c.c.
0·4008	+476·6°	−0·3°	Cd_{5086}	±476·9°	+1·8°	−478·7°	0·4000
,,	432·1	+0·2	Ag_{5209}	431·9	−0·4	431·5	,,
,,	359·4	−0·3	Hg_{5461}	359·7	+1·6	361·3	,,
,,	294·4	+0·4	Hg_{5780}	294·0	−1·5	292·5	,,
,,	275·7	+0·3	Na_{5893}	275·4	−0·4	275·0	,,
,,	245·8	±0	Li_{6104}	245·8	−0·8	245·0	,,
,,	208·4	−0·2	Cd_{6438}	208·6	−1·1	207·5	,,
,,	184·7	−0·3	Li_{6708}	185·0	±0	185·0	,,

The solution exhibited slight mutarotation ; the initial value $[\alpha]_{Hg_{gr}} = 359 \cdot 4°$ and $[\alpha]_{Hg_y} = 294 \cdot 4°$ changing to 349·4° and 284·4° respectively in course of 24 hours.

TABLE XV. p-*Chloranilinomethylenecamphor in acetone.*

$$[\alpha] = \pm \frac{70{\cdot}58}{\lambda^2 - 0{\cdot}1228}\,;\ \lambda_0 = 0{\cdot}3504.$$

Dextro			Line	Calc. $[\alpha]$ c	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]$ o	o–c			o'–c	Obs. $[\alpha]$ o'	Concentration g./100 c.c.
0·4020	+518·7°	−0·7°	Cd_{5086}	±519·4°	+0·6°	−520·0°	0·4000
,,	476·4	+1·2	Ag_{5209}	475·2	+1·1	476·3	,,
,,	401·8	−0·6	Hg_{5461}	402·4	−1·1	401·3	,,
,,	334·7	+0·7	Hg_{5780}	334·0	+1·0	335·0	,,
,,	313·4	−1·0	Na_{5893}	314·4	−0·6	313·8	,,
,,	282·3	−0·3	Li_{6104}	282·6	−0·1	282·5	,,
,,	242·5	+0·5	Cd_{6438}	242·0	+0·5	242·5	,,
,,	216·4	+0·7	Li_{6708}	215·7	−0·7	215·0	,,

The solution did not exhibit mutarotation.

TABLE XVI. p-*Chloranilinomethylenecamphor in ethyl alcohol.*

$$[\alpha] = \pm \frac{73{\cdot}20}{\lambda^2 - 0{\cdot}1180}\,;\ \lambda_0 = 0{\cdot}3435.$$

Dextro			Line	Calc. $[\alpha]$ c	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]$ o	o–c			o'–c	Obs. $[\alpha]$ o'	Concentration g./100 c.c.
0·4000	+650·0°	−1·2°	Cd_{4800}	±651·2°	−0·7°	−650·5°	0·4028
,,	518·8	−1·4	Cd_{5086}	520·2	−0·1	520·1	,,
,,	478·8	+1·3	Ag_{5209}	477·5	+1·0	478·5	,,
,,	406·3	+0·1	Hg_{5461}	406·2	−0·2	406·0	,,
,,	338·8	+0·1	Hg_{5780}	338·7	+0·2	338·7	,,
,,	318·8	−0·4	Na_{5892}	319·2	−0·4	318·8	,,
,,	287·5	±0	Li_{6104}	287·5	+0·5	288·0	,,
,,	246·3	−0·6	Cd_{6438}	246·9	−1·1	245·8	,,
,,	221·3	+0·8	Li_{6708}	220·5	+0·5	221·0	,,

The solution did not exhibit mutarotation.

TABLE XVII. p-*Chloranilinomethylenecamphor in pyridine.*

$$[\alpha] = \pm \frac{68 \cdot 19}{\lambda^2 - 0 \cdot 1251}; \quad \lambda_0 = 0 \cdot 3537.$$

Dextro			Line	Calc. $[\alpha]$ c	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]$ o	$o-c$			$o'-c$	Obs. $[\alpha]$ o'	Concentration g./100 c.c.
0·4028	+645·8°	−1·8°	Cd_{4800}	±647·6	..	..	0·4004
,,	510·5	+0·1	Cd_{5086}	510·4	−0·8°	−509·6°	,,
,,	465·7	−0·7	Ag_{5209}	466·4	−0·6	465·8	,,
,,	394·4	+0·5	Hg_{5461}	393·9	+0·8	394·7	,,
,,	326·7	+0·5	Hg_{5780}	326·2	−0·2	326·0	,,
,,	306·6	−0·3	Na_{5892}	306·9	+0·3	307·2	,,
,,	275·8	+0·3	Li_{6104}	275·5	−0·8	274·7	,,
,,	234·7	−0·9	Cd_{6438}	235·6	+0·4	236·0	,,
,,	209·8	±0	Li_{6708}	209·8	±0	209·8	,,

The solution did not exhibit mutarotation.

TABLE XVIII. p-*Chloranilinomethylenecamphor in methyl alcohol.*

$$[\alpha] = \pm \frac{75 \cdot 34}{\lambda^2 - 0 \cdot 1178}; \quad \lambda_0 = 0 \cdot 3432.$$

Dextro			Line	Calc. $[\alpha]$ c	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]$ o	$o-c$			$o'-c$	Obs. $[\alpha]$ o'	Concentration g./100 c.c.
0·4012	+668·0°	−1·1°	Cd_{4800}	+669·1°	..	..	0·4040
,,	534·6	−0·1	Cd_{5086}	534·7	+1·2°	−535·9°	,,
,,	492·3	+1·5	Ag_{5209}	490·8	−0·7	490·1	,,
,,	417·7	±0	Hg_{5461}	417·7	+0·3	418·0	,,
,,	347·7	−0·5	Hg_{5780}	348·2	−0·1	348·1	,,
,,	327·9	−0·4	Na_{5892}	328·3	+0·9	329·2	,,
,,	296·6	+1·0	Li_{6104}	295·6	+1·4	297·0	,,
,,	254·2	+0·2	Cd_{6438}	254·0	+1·0	255·0	,,
,,	226·8	±0	Li_{6708}	226·8	−0·3	226·5	,,

The solution did not exhibit mutarotation.

TABLE XIX. 2 : 4-*Dichloranilinomethylenecamphor in acetone.*

$$[\alpha] = \pm \frac{58{\cdot}84}{\lambda^2 - 0{\cdot}1353}; \ \lambda_0 = 0{\cdot}3678.$$

Dextro			Line	Calc. [α] *c*	*Lævo*		
Concentration g./100 c.c.	Obs. [α] *o*	*o–c*			*o′–c*	Obs. [α] *o′*	Concentration g./100 c.c.
0·4016	+617·4°	−1·3°	Cd_{4800}	±618·7°	..	..	0·4040
,,	476·9	±0	Cd_{5086}	476·9	+0·9°	−477·8°	,,
,,	432·0	−0·7	Ag_{5209}	432·7	−2·0	430·7	,,
,,	362·3	+1·1	Hg_{5461}	361·2	+0·2	361·4	,,
,,	296·4	+0·3	Hg_{5780}	296·1	+0·9	297·0	,,
,,	277·7	±0	Na_{5893}	277·7	−0·2	277·5	,,
,,	248·9	+0·9	Li_{6104}	248·0	+0·8	248·8	,,
,,	210·5	−0·2	Cd_{6438}	210·7	−1·5	209·2	,,
,,	188·0	+0·9	Li_{6708}	187·1	−0·2	186·9	,,

The solution did not exhibit mutarotation.

TABLE XX. 2 : 4-*Dichloranilinomethylenecamphor in chloroform.*

$$[\alpha] = \pm \frac{58{\cdot}84}{\lambda^2 - 0{\cdot}1380}; \ \lambda_0 = 0{\cdot}3715.$$

Dextro			Line	Calc. [α] *c*	*Lævo*		
Concentration g./100 c.c.	Obs. [α] *o*	*o–c*			*o′–c*	Obs. [α] *o′*	Concentration g./100 c.c.
0·4024	+489·6°	+2·1°	Cd_{5086}	± 487·5°	+1·3°	−488·8°	0·4000
,,	441·2	−0·3	Ag_{5209}	441·5	+1·0	442·5	,,
,,	366·6	−0·8	Hg_{5461}	367·4	−1·1	366·3	,,
,,	300·8	+0·7	Hg_{5780}	300·1	−0·1	300·0	,,
,,	282·1	+0·9	Na_{5893}	281·2	−0·2	280·0	,,
,,	249·8	−1·0	Li_{6104}	250·8	+0·5	251·3	,,
,,	212·5	−0·3	Cd_{6438}	212·8	−0·3	212·5	,,
,,	188·9	+0·3	Li_{6708}	188·6	+0·2	188·8	,,

The solution did not exhibit mutarotation.

TABLE XXI. 2 : 4-*Dichloranilinomethylenecamphor in pyridine.*

$$[\alpha] = \pm \frac{58 \cdot 84}{\lambda^2 - 0 \cdot 1380}\ ;\ \lambda_0 = 0 \cdot 3715.$$

Dextro			Line.	Calc. $[\alpha]$ c	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]$ o	$o-c$			$o'-c$	Obs. $[\alpha]$ o'	Concentration g./100 c.c.
0·4024	+635·1°	−1·7°	Cd_{4800}	±636·8°	+0·7°	−637·5°	0·4000
,,	488·4	+0·9	Cd_{5086}	487·5	±0	487·5	,,
,,	441·2	−0·3	Ag_{5209}	441·5	−1·5	440·0	,,
,,	367·9	+0·5	Hg_{5461}	367·4	−1·1	366·3	,,
,,	300·7	+0·6	Hg_{5780}	300·1	+1·1	301·2	,,
,,	280·9	−0·3	Na_{5893}	281·2	±0	281·2	,,
,,	251·1	+0·3	Li_{6104}	250·8	+0·4	251·2	,,
,,	212·5	−0·3	Cd_{6438}	212·8	−1·5	211·3	,,
,,	188·9	+0·3	Li_{6708}	188·6	+0·2	188·8	,,

The dispersion formula is the same as that of the chloroform solution. The solution did not exhibit mutarotation.

TABLE XXII. 2 : 4-*Dichloranilinomethylenecamphor in benzene.*

$$[\alpha] = \pm \frac{53 \cdot 14}{\lambda^2 - 0 \cdot 1407}\ ;\ \lambda_0 = 0 \cdot 3751.$$

Dextro			Line	Calc. $[\alpha]$ c	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]$ o	$o-c$			$o'-c$	Obs. $[\alpha]$ o'	Concentration g./100 c.c.
0·4040	+449·5°	−0·8°	Cd_{5086}	±450·3°	+0·4°	−450·7°	0·4016
,,	408·4	+1·3	Ag_{5209}	407·1	+0·1	407·2	,,
,,	337·9	+0·5	Hg_{5461}	337·4	±0	337·4	,,
,,	273·6	−1·1	Hg_{5780}	274·7	−2·0	272·7	,,
,,	257·4	+0·1	Na_{5893}	257·3	−0·8	256·5	,,
,,	228·9	−0·2	Li_{6104}	229·1	±0	229·1	,,
,,	194·3	+0·2	Cd_{6438}	194·1	+0·1	194·2	,,
,,	172·0	+0·2	Li_{6708}	171·8	±0	171·8	,,

The solution did not exhibit mutarotation.

TABLE XXIII. 2 : 4-*Dichloranilinomethylenecamphor in ethyl alchol.*

$$[\alpha] = \pm \frac{59{\cdot}55}{\lambda^2 - 0{\cdot}1373}; \quad \lambda_0 = 0{\cdot}3705.$$

Dextro			Line	Calc. [α] *c*	*Lævo*		
Concentration g./100 c.c.	Obs. [α] *o*	*o–c*			*o'–c*	Obs. [α] *o'*	Concentration g./100 c.c.
0·4048	+637·5°	−2·1°	Cd_{4800}	±639·6°	+0·5°	−640·1°	0·4024
,,	491·5	+0·9	Cd_{5086}	490·6	−0·9	489·7	,,
,,	445·8	+1·3	Ag_{5209}	444·5	+1·7	446·2	,,
,,	369·3	−0·9	Hg_{5461}	370·2	−1·0	369·2	,,
,,	302·6	−0·4	Hg_{5780}	302·6	−0·6	302·0	,,
,,	284·1	+0·4	Na_{5893}	283·7	+0·8	284·5	,,
,,	253·2	+0·1	Li_{6104}	253·1	+0·4	253·5	,,
,,	213·7	−1·1	Cd_{6438}	214·8	−1·0	213·8	,,
,,	189·5	−1·0	Li_{6708}	190·5	−0·4	190·1	,,

The solution did not exhibit mutarotation.

TABLE XXIV. 2 : 4-*Dichloranilinomethylenecamphor in methyl alchol.*

$$[\alpha] = \pm \frac{56{\cdot}09}{\lambda^2 - 0{\cdot}1432}; \quad \lambda_0 = 0{\cdot}3784.$$

Dextro			Line	Calc. [α] *c*	*Lævo*		
Concentration g./100 c.c.	Obs. [α] *o*	*o–c*			*o'–c*	Obs. [α] *o'*	Concentration g./100 c.c.
0·4000	+485·0°	−0·5°	Cd_{5086}	±485·5°	−0·3°	−485·2°	0·4040
,,	438·7	+0·8	Ag_{5209}	437·9	+0·2	438·1	,,
,,	362·5	+0·6	Hg_{5461}	361·9	+0·8	362·7	,,
,,	292·5	−1·3	Hg_{5780}	293·8	−0·4	293·4	,,
,,	273·8	−1·1	Na_{5893}	274·9	−0·1	274·8	,,
,,	245·0	+0·5	Li_{6104}	244·5	+0·6	245·1	,,
,,	207·5	+0·7	Cd_{6438}	206·8	−0·2	206·6	,,
,,	182·5	−0·3	Li_{6708}	182·8	+0·4	183·2	,,

The solution did not exhibit mutarotation.

TABLE XXV. 2 : 4 : 6-*Trichloranilinomethylenecamphor in acetone.*

$$[\alpha] = \pm \frac{43 \cdot 39}{\lambda^2 - 0 \cdot 1297}; \quad \lambda_0 = 0 \cdot 3601.$$

Dextro			Line	Calc. $[\alpha]$ c	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]$ o	$o-c$			$o'-c$	Obs. $[\alpha]$ o'	Concentration g./100 c.c.
0·4020	+430·3°	−0·6°	Cd_{4800}	±430·9°	−0·9°	−430·0°	0·4000
,,	337·2	+0·8	Cd_{5086}	336·4	−0·1	336·3	,,
,,	306·0	−0·4	Ag_{5209}	306·4	+1·1	307·5	,,
,,	258·7	+1·2	Hg_{5461}	257·5	±0	257·5	,,
,,	211·5	−0·8	Hg_{5780}	212·3	−1·0	211·3	,,
,,	200·3	+0·9	Na_{5893}	199·4	+1·8	201·2	,,
,,	179·1	+0·4	Li_{6104}	178·7	+0·1	178·8	,,
,,	151·8	−0·5	Cd_{6438}	152·3	−1·0	151·3	,,
,,	135·6	+0·1	Li_{6708}	135·5	+0·8	136·3	,,

The solution did not exhibit mutarotation.

Table XXVI. 2 : 4 : 6-*Trichloranilinomethylenecamphor in chlorofrom.*

$$[\alpha] = \pm \frac{42 \cdot 66}{\lambda^2 - 0 \cdot 1304}; \quad \lambda_0 = 0 \cdot 3611.$$

Dextro			Line	Calc. $[\alpha]$ c	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]$ o	$o-c$			$o'-c$	Obs. $[\alpha]$ o'	Concentration g./100 c.c.
0·4000	+425·0°	−1·6°	Cd_{4800}	±426·6°	−2·1°	−425·4°	0·4032
,,	332·5	±0	Cd_{5086}	332·5	+1·1	333·6	,,
,,	302·5	−0·2	Ag_{5209}	302·7	−1·2	301·5	,,
,,	255·0	+0·8	Hg_{5461}	254·2	+1·3	255·5	,,
,,	208·8	−0·6	Hg_{5780}	209·4	+0·3	209·7	,,
,,	197·5	+0·8	Na_{5893}	196·7	+0·6	197·3	,,
,,	176·3	+0·2	Li_{6104}	176·1	+1·2	177·3	,,
,,	150·0	−0·1	Cd_{6438}	150·1	−0·1	150·0	,,
,,	132·8	−0·7	Li_{6708}	133·5	−0·8	132.7	,,

The solution did not exhibit mutarotation.

TABLE XXVII. 2 : 4 : 6-*Trichloranilinomethylenecamphor in benzene.*

$$[\alpha] = \pm \frac{32 \cdot 72}{\lambda^2 - 0 \cdot 1483}; \quad \lambda_0 = 0 \cdot 3851.$$

Dextro			Line	Calc. $[\alpha]$ c	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]$ o	$o-c$			$o'-c$	Obs. $[\alpha]$ o'	Concentration g./100 c.c.
0·4012	+295·4°	−1·0°	Cd_{5086}	±296·4°	−1·8°	−294·6°	0·4040
,,	265·5	−0·5	Ag_{5209}	266·0	+0·2	266·2	,,
,,	219·1	+0·8	Hg_{5461}	218·3	+0·7	219·0	,,
,,	175·8	−0·3	Hg_{5780}	176·1	−0·3	175·8	,,
,,	164·5	+0·1	Na_{5893}	164·4	+1·3	165·7	,,
,,	145·8	−0·1	Li_{6104}	145·9	+0·2	146·1	,,
,,	123·4	+0·5	Cd_{6438}	122·9	−0·3	122·6	,,
,,	108·5	±0	Li_{6708}	108·5	+0·3	108·8	,,

The solution did not exhibit mutarotation.

TABLE XXVIII. 2 : 4 : 6-*Trichloranilinomethylenecamphor in pyridine.*

$$[\alpha] = \pm \frac{41 \cdot 70}{\lambda^2 - 0 \cdot 1315}; \quad \lambda_0 = 0 \cdot 3626.$$

Dextro			Line	Calc. $[\alpha]$ c	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]$ o	$o-c$			$o'-c$	Obs. $[\alpha]$ o'	Concentration g./100 c.c.
0·4008	+326·8°	−1·0°	Cd_{5086}	±327·8°	+0·3°	−328·1°	0·4024
,,	299·4	+1·6	Ag_{5209}	298·2	−0·4	297·8	,,
,,	250·8	+0·7	Hg_{5461}	250·1	+0·9	251·0	,,
,,	205·6	−0·1	Hg_{5780}	205·7	−0·6	205·1	,,
,,	192·2	−1·0	Na_{5893}	193·2	+0·6	193·8	,,
,,	173·4	+0·5	Li_{6104}	172·9	−0·1	172·8	,,
,,	147·1	−0·2	Cd_{6438}	147·3	−0·6	146·7	,,
,,	131·0	±0	Li_{6708}	131·0	−0·5	130·5	,,

The solution did not exhibit mutarotation.

TABLE XXIX. 2 : 4 : 6-*Trichloranilinomethylenecamphor in ethyl alcohol.*

$$[\alpha] = \pm \frac{41 \cdot 46}{\lambda^2 - 0 \cdot 1422}; \quad \lambda_0 = 0 \cdot 3771.$$

Dextro			Line	Calc. $[\alpha]$	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]$ o	$o-c$		c	$o'-c$	Obs. $[\alpha]$ o'	Concentration g./100 c.c.
0·4016	+354·9°	−1·0°	Cd_{5086}	±355·9°	−2·1°	−353·8°	0·4000
,,	321·2	+1·1	Ag_{5209}	320·1	+1·2	321·3	,,
,,	265·2	−0·6	Hg_{5461}	265·8	−0·8	265·0	,,
,,	216·7	+0·6	Hg_{5780}	216·1	+0·2	216·3	,,
,,	201·8	−0·3	Na_{5893}	202·1	−0·8	201·3	,,
,,	179·3	−0·6	Li_{6104}	179·9	−1·1	178·8	,,
,,	153·0	+0·7	Cd_{6438}	152·3	+0·2	152·5	,,
,,	134·5	−0·2	Li_{6708}	134·7	+0·3	135·0	,,

The solution did not exhibit mutarotation.

TABLE XXX. 2 : 4 : 6-*Trichloranilinomethylenecamphor in methyl alcohol.*

$$[\alpha] = \pm \frac{41 \cdot 76}{\lambda^2 - 0 \cdot 1372}; \quad \lambda_0 = 0 \cdot 3704.$$

Dextro			Line	Calc. $[\alpha]$	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]$ o	$o-c$		c	$o'-c$	Obs. $[\alpha]$ o'	Concentration g./100 c.c.
0·4004	+343·5°	−0·2°	Cd_{5086}	±343·7°	+2·4°	−346·1°	0·4032
,,	312·2	±0	Ag_{5209}	312·2	+0·3	312·5	,,
,,	259·8	+0·4	Hg_{5461}	259·4	−0·3	259·1	,,
,,	212·3	+0·2	Hg_{5780}	212·1	−0·1	212·0	,,
,,	197·4	−1·5	Na_{5893}	198·9	+0·7	199·6	,,
,,	178·6	+1·2	Li_{6104}	177·4	±0	177·4	,,
,,	149·9	−0·9	Cd_{6438}	150·8	−0·7	150·1	,,
,,	133·6	+0·1	Li_{6708}	133·5	+0·4	133·9	,,

The solution did not exhibit mutarotation.

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